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THE UNIVERSITY OF ALBERTA

THE REACTIVITIES OF CHARCOAL

by

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2

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ABSTRACT

The oxidation of charcoal by carbon dioxide has been used to examine the differences in reactivity of a series of steam activated coconut charcoals. Several mechanisms have already been proposed for this reaction and an attempt has been made to reconcile the two most plausible ones by incorporating a term depending on the surface. The experimental work indicated that these two mechanisms were particular cases applying to either highly steam activated and hence smooth, but highly porous charcoals, or unactivated and hence rough, moderately porous charcoals. Steam activation also had the effect of reducing the reaction rate of the charcoal. It has been concluded that quantitative work along these lines should be carried out on a pure carbon and a method to characterize the reactive portions of its surface would have to be developed.

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I INTRODUCTION

About two years ago, the Research Council of Alberta initiated an enquiry into the fundamental processes occurring during the combustion of a particle of pulverized coal. Ideally, this combustion may be divided into three phases, a pre-ignition zone, an ignition zone and a combustion zone. The partial processes occurring are recognized as thermodynamical, i.e. gas kinetics, heat and mass transfer; physico-chemical, i.e. reaction kinetics and equilibria; thermophysical, i.e. behaviour of the coal, ash and slag at high temperature; and aerodynamical, i.e. the flow of air, gas and dust suspensions and the relative velocities between the solid and the gas. Furthermore, there are complications due to swelling, coking and the evolution of volatiles. The mathematical models extant invariably were oversimplified, assuming a sphere of pure carbon. Further, they were still semi-empirical because an arbitrary mechanism was used to develop the rate equation. The test of whether a velocity constant or group of constants was significant or not, was made by fitting the derived curve to the experimental data and assuming that all the factors causing deviation were negligible. Another major inadequacy in these models was that in the chemically controlled zone of reaction no satisfactory provision was made for the different reactivities of the different

carbons studied. It seemed, therefore, a worthwhile task to examine the reactivities of a series of charcoals on which this laboratory had obtained some information (Habgood and Hanlan (17)). For further simplicity it was decided to study the reaction of carbon dioxide (rather than oxygen) with charcoal because this would involve one less gaseous species. Since the measurements were to be in the chemically controlled zone, a flow system with a fixed charcoal bed was considered to be suitable for the experiments.

II LITERATURE REVIEW

Introduction

The literature on the mechanism of the reduction of carbon dioxide by carbon spans fifty years with the recognition of the vital role played by the solid phase being confined to the last few. Rather than present the survey in a purely chronological order, the subject matter of the earlier period has been subdivided into the following topics:

1. The effect of gas phase concentrations;
2. Exchange reactions with the surface;
3. Adsorption of components on the surface;
4. The role of surface oxide(s).

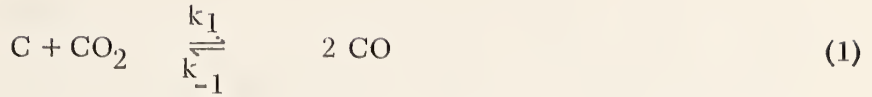
The postulated mechanisms are then critically examined and the concept of sites of either different reactivities or different natures introduced. The evidence demonstrating the influence of the solid phase on the reaction rate is then discussed.

The Effect of Gas Phase Concentrations

The equilibrium ratio at constant pressure, A_p^* , given by $A_p = P_{CO_2}/P_{CO}^2$, has been found to vary, e.g. at 746°C, Broom and Travers (5) found that A_p varied between 0.225 and 0.37, the variation depending on heat treatment, and increasing with graphitization. Oming and Sterling (26) found also that A_p varied with gas composition and the state of oxidation of the carbon surface.

* A_p is different from the equilibrium constant K_p and is inversely proportional to it.

The over-all reaction is given by:



where k_1 is the rate constant of the forward reaction and k_{-1} is the rate constant of the reverse reaction.

The equilibrium constant

$$K_p = \frac{k_1}{k_{-1}} = \frac{P_{\text{CO}}^2}{(\text{C}) P_{\text{CO}_2}} \quad (2)$$

where (C) is the concentration of the carbon. From equation (2)

$$\frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = K_p (\text{C}) \quad (3)$$

For the ratio $P_{\text{CO}}^2/P_{\text{CO}_2}$ to vary, (C) must vary and thus some kind of concentration term for the solid phase must be introduced. The reaction is then considered to take place on active sites and (C) will represent their concentration and will have to vary with heat treatment and the state of oxidation of the surface in order to fit the experimental evidence.

Reif (28,29), Gadsby et al (15) and Blackwood and Ingeme(1) found a strong inhibition by carbon monoxide, with the fractional reduction in rate for a given increase in the partial pressure of carbon monoxide being more marked the lower the temperature.

The reaction order varied from zero to one depending on temperature, pressure, type of carbon, purity of carbon and the geometric dimensions of the sample, Walker et al (41).

- e.g. 1. Gadsby et al (15) found a fractional order for a coconut charcoal reacted over a temperature range of 700 – 830°C.
2. Brown (6) found a zero order reaction for partial pressures of carbon dioxide above 3 cm . mercury at 600°C.
3. Blackwood and Ingeme(1) found almost a first order reaction at 870°C and low carbon monoxide partial pressures, whereas at lower temperatures and higher carbon monoxide partial pressures, the rate increased with increasing carbon dioxide partial pressure to an exponent greater than unity.

There is general agreement by Walker et al (41), Semechkova and Frank Kamenetzky (31), Gadsby et al (15), Reif (29), and Ergun (11), that the experimental data on the rate of gasification fit an equation of the form:

$$R = \frac{K_1 P_{CO_2}}{1 + K_2 P_{CO} + K_3 P_{CO_2}} \quad (4)$$

where R = rate of reaction in gm . mol . C . gasified per gm . mol . C per sec . , K_1 , K_2 , and K_3 are reaction parameters. However, in a series of experiments ranging up to a pressure of 40 atm . of carbon dioxide, an extra term was found to be needed by Blackwood and Ingeme (1), e.g.

$$R = \frac{K_1 P_{CO_2} + K_4 P_{CO_2}^2}{1 + K_2 P_{CO} + K_3 P_{CO_2}} \quad (5)$$

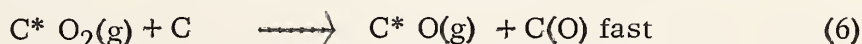
K_4 , dependent on the rate constants of the component reactions, was introduced because when P_{CO_2}/R was plotted against the partial pressure of carbon monoxide for various partial pressures of carbon dioxide, a series of parallel

straight lines was not obtained as would be expected from equation (4), but the lines intersected almost on the ordinate. It was assumed that the $K_4 P_{CO_2}^2$ term becomes negligible at atmospheric pressure.

Exchange Reactions with the Surface

The experiments described in this section were conducted using carbon fourteen designated C*.

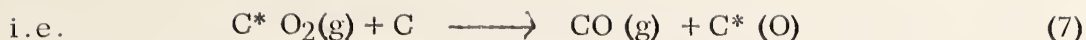
Bonner and Turkevich (3), in a series of experiments in which carbon dioxide and the carbon monoxide formed were continuously recirculated over a char, found that initially there was no exchange between the carbon monoxide gas and the surface, i.e.



However, eventually one-fifth of the C* disappeared from the product gas and was found on the char surface. This may be due to the slow attainment of an adsorption equilibrium between carbon monoxide in the gas phase and condensed on the surface, which also explains why no further exchange occurred between the carbon monoxide and the surface on long contact at the end of an experiment.

Orning and Sterling (26) found at the end of a flow experiment (not recirculating), that no active carbon was found on the char surface. This may have been because the active carbon monoxide formed was swept away and the experiment discontinued before a detectable amount could be accumulated on the surface.

Brown (6) reported that a small fraction, e.g. 1 - 2% of the reacting carbon dioxide molecules deposited their carbon atoms on the surface,



Adsorption of Components on Surface

While carbon dioxide does not appear to be adsorbed on carbon above 600°C. (31), carbon monoxide is adsorbed when admitted to a degassed coke. According to Gadsby et al. (15), the adsorption isotherm is roughly independent of temperature, but retardation of the reduction of carbon dioxide by carbon due to carbon monoxide decreased rapidly with increasing temperature. If the carbon monoxide molecules were being adsorbed on the same sites as those on which the carbon dioxide molecules were being reduced, and the number of them adsorbed does not vary appreciably with changing temperature (this is known because the adsorption isotherm was roughly independent of temperature), then the retardation of the reaction by carbon monoxide would be expected to remain fairly constant. Consequently, as the inhibition decreased rapidly with increasing temperature, it may be deduced that the carbon monoxide was also adsorbed on less active parts of the surface and may not be adsorbed on the sites where reaction takes place. Supporting the view that carbon monoxide is adsorbed on different sites from those upon which reaction takes place is the evidence supplied by Reif (29) that for a high temperature coke, only one-fifth of the surface capable of taking up oxygen from carbon dioxide was capable of adsorbing carbon monoxide. The fractional surface coverage, however, varies widely from carbon to carbon because the same author in (28) cites a surface coverage by carbon monoxide, as determined by the B.E.T. method, of 75% of the total. Walker (38) also found that the adsorption of carbon monoxide was a side reaction not taking part in the gasification.

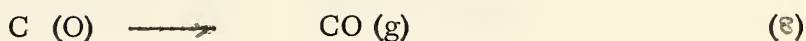
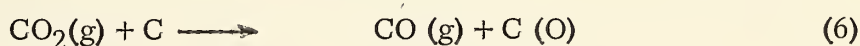


The evidence therefore indicates that the carbon monoxide is adsorbed on different sites from those upon which the reaction takes place and also that the number of sites varies greatly with the carbon.

The Role of Surface Oxide(s)

(a) The Formation and Removal of Surface Oxides - The complex formed when carbon monoxide is adsorbed on carbon may be considered as an oxide. Its formation has already been discussed. Reif (29) found that it was more readily desorbed by pumping off at higher temperatures than lower ones and concluded that it was more stable at the lower temperatures.

Bonner and Turkevich (3) found that when carbon dioxide reacted with carbon, initially 95% of the carbon dioxide was found to convert quickly to carbon monoxide in a 1:1 molecular ratio (i.e. no pressure increase was observed experimentally), followed by a slow evolution of carbon monoxide. Semechkova and Frank Kamenetzky (31), Langmuir (22) and Broom and Travers (5) reported qualitatively similar results. The reactions occurring will be:



C(O) represents some kind of surface oxide. Gadsby et al (15) found that during reaction the adsorbed oxygen, i.e. the oxygen bound in these complexes, increased to a maximum and then remained constant.

(b) The Effect of the Surface Oxides - Brown (6) found that for graphite, oxygen pretreatment caused a two-fold increased reaction rate with the enhanced reactivity remaining after subsequent reduction with hydrogen. The

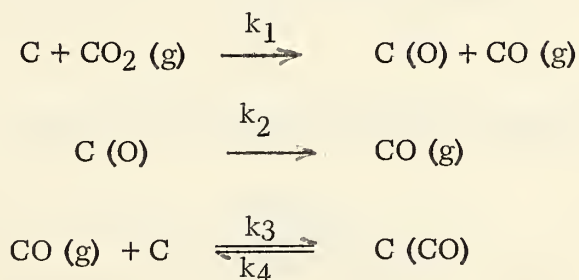
phenomenon was consequently ascribed to etching of the surface and this explained also the absence of an enhancement of reaction rate when sugar charcoal, which already had a highly irregular surface, was treated similarly. However, Broom and Travers (5) found that during the early stages of reaction on a previously cleaned carbon surface, the oxide on the surface had the effect of diminishing the rate of reduction almost linearly with the surface concentration with the influence of the oxygen on the surface also depending on how long it had been there. This implies that an oxygenated site is not as active as a non-oxygenated one and is compatible with the scheme already postulated, i.e. equations (6) and (8) where (6) occurs much faster than (8).

MECHANISMS

The foregoing experimental evidence has been used to arrive at various mechanisms which are reviewed next.

Mechanism I

(Gadsby et al (14))



It can be seen that two kinds of complex were assumed but the sites were considered equivalent with each one capable of adsorbing one oxygen atom or carbon monoxide molecule and one new site being formed as a result of the second reaction.

Let the fraction of sites covered by (O) be Θ_1

Let the fraction of sites covered by (CO) be Θ_2

At the steady reaction rate, there will be a balance on these surface species:

$$k_1 P_{CO_2} (1 - \Theta_1 - \Theta_2) = k_2 \Theta_1 \quad (1)$$

$$k_3 P_{CO} (1 - \Theta_1 - \Theta_2) = k_4 \Theta_2 \quad (2)$$

$$k_1 k_4 \Theta_2 P_{CO_2} = k_2 k_3 \Theta_1 P_{CO} \quad (3)$$

$$\text{from (1) } \Theta_2 = 1 - \Theta_1 - \frac{k_2 \Theta_1}{k_1 P_{CO_2}} \quad (4)$$

$$(3) \text{ and (4) give } \frac{k_2 k_3 \Theta_1 P_{CO}}{k_1 k_4 P_{CO_2}} = 1 - \Theta_1 - \frac{k_2 \Theta_1}{k_1 P_{CO_2}}$$

$$\therefore \Theta_1 = \frac{1}{\frac{k_2 k_3 P_{CO}}{k_1 k_4 P_{CO_2}} + \frac{k_2 + 1}{k_1 P_{CO_2}}}$$

The rate of reaction $R = k_2 \Theta_1$

$$R = \frac{k_1 P_{CO_2}}{1 + \frac{k_3 P_{CO}}{k_4} + \frac{k_1 P_{CO_2}}{k_2}}$$

This may be compared with the equation

$$R = \frac{K_1 P_{CO_2}}{1 + K_2 P_{CO} + K_3 P_{CO_2}}$$

given earlier.

$$\text{here } k_1 = K_1$$

$$k_3/k_4 = K_2$$

$$k_1/k_2 = K_3$$

$$= \frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} \right) = \frac{1}{2}$$

$$= \frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} \right) = \frac{1}{2}$$

$$= \frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} \right) = \frac{1}{2}$$

$$= \frac{1}{2}$$

$$(1) \quad \frac{1}{2} = \frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} \right) = \frac{1}{2}$$

$$(2) \quad \frac{1}{2} = \frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} \right) = \frac{1}{2}$$

$$(3) \quad \frac{1}{2} = \frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} \right) = \frac{1}{2}$$

$$(4) \quad \frac{1}{2} = \frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} \right) = \frac{1}{2}$$

$$\frac{1}{2} = \frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} \right) = \frac{1}{2}$$

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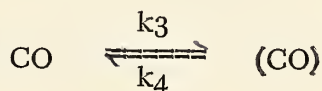
$$= \frac{1}{2}$$

$$= \frac{1}{2}$$

$$= \frac{1}{2}$$

$$= \frac{1}{2}$$

The reactions considered in this mechanism are all compatible with the experimental evidence presented earlier. However, the scheme does not allow for the different reactivities of different carbons. In particular, the coefficient of the P_{CO} term, K_2 , is the equilibrium constant of the adsorption:



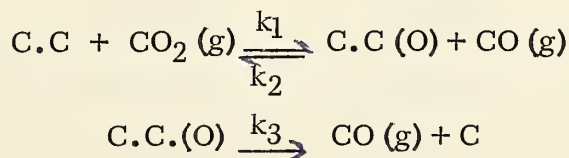
and hence should be constant for different carbons if the postulation of equivalent sites is correct. Reif (29) tabulated some values of K_2 obtained by different investigators.

Reference	$K_2 \text{ atm}^{-1}$
Gadsby et al (15)	$10^{-7.9} e^{45,500/RT}$
Lewis et al (24)	$10^{-1.9} e^{15,400/RT}$
Wu (44)	$10^{-5.4} e^{40,300/RT}$
Wu (44)	$10^{-8.5} e^{60,000/RT}$

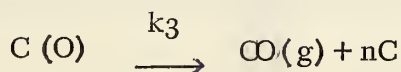
It can be seen that there is little agreement.

Mechanism II

(Reif (29), Ergun (11))



Only one kind of site was postulated. Ergun (11) considered the reaction



but assumed n averages 1.

A balance on C (O) at the steady reaction rate gives

$$k_1 (1 - \Theta) P_{CO_2} - k_2 \Theta P_{CO} - k_3 \Theta = 0$$

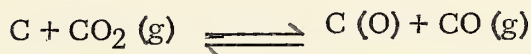
$$\Theta = \frac{k_1 P_{CO_2}}{k_3 + k_2 P_{CO} + k_1 P_{CO_2}}$$

$$\text{Rate of reaction } R = k_3 \Theta$$

$$= \frac{k_1 k_3 P_{CO_2}}{k_3 + k_2 P_{CO} + k_1 P_{CO_2}}$$

$$R = \frac{k_1 P_{CO_2}}{1 + \frac{k_2}{k_3} P_{CO} + \frac{k_1}{k_3} P_{CO_2}} \quad \text{cf. } R = \frac{K_1 P_{CO_2}}{1 + K_2 P_{CO} + K_3 P_{CO_2}}$$

$$\frac{k_1}{k_2} = \frac{K_3}{K_2} = \text{equilibrium constant of reaction:}$$



The ratio of these two coefficients should thus be constant.

Reif (29) tabulated values of K_2 and K_3 obtained by different investigators.

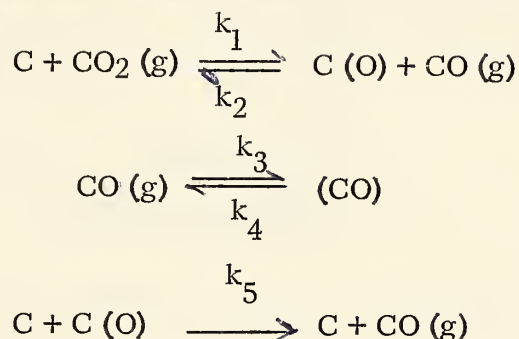
Reference	K_2 at -1	K_3 at -1	K_3/K_2
Gadsby et al (15)	$10^{-7.9} e^{45,500/RT}$	$10^{6.5} e^{-30,100/RT}$	$10^{14.4} e^{-75,600/RT}$
Lewis et al (24)	$10^{-1.9} e^{15,400/RT}$	$10^{-0.6} e^{6,400/RT}$	$10^{1.3} e^{-9,000/RT}$
Wu (41)	$10^{-5.4} e^{40,300/RT}$	$10^{-1.5} e^{6,100/RT}$	$10^{3.9} e^{-34,200/RT}$
Wu (44)	$10^{-8.5} e^{60,600/RT}$	$10^{-0.8} e^{6,600/RT}$	$10^{7.8} e^{-54,000/RT}$

Again there appears to be no agreement. It can also be seen

that there is no way for carbon monoxide gas to be adsorbed on the surface by this mechanism.

Mechanism III

(Semechkova and Frank Kamenetzky (31))



This mechanism allows for two kinds of surface complex but only one kind of site. Two cases were considered, viz reaction on a fresh surface and reaction at the steady state.

The steady state reaction is given by

$$R = 2 \frac{k_1 k_4 P_{\text{CO}_2} - k_3 k_2 P_{\text{CO}}^2}{k_1 P_{\text{CO}_2} + k_3 P_{\text{CO}} + k_4 + k_2 P_{\text{CO}}}$$

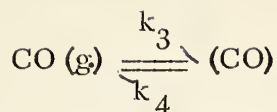
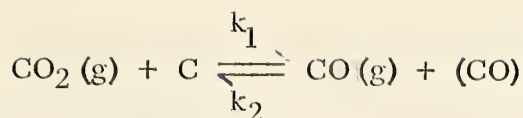
In order to fit the rate equation

$$R = \frac{K_1 P_{\text{CO}_2}}{1 + K_2 P_{\text{CO}} + K_3 P_{\text{CO}_2}}$$

Gadsby et al (14) showed that the scheme of equations had to reduce to either of those two postulated previously and consequently the mechanism is subject to the same criticisms.

Mechanism IV

(Evropin et al (13))



This mechanism has one surface complex and one type of site. Reif (8) showed this scheme was unable to reduce to

$$R = \frac{K_1 P_{\text{CO}_2}}{1 + K_2 P_{\text{CO}} + K_3 P_{\text{CO}_2}}$$

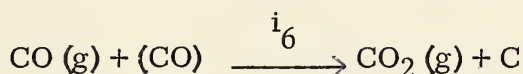
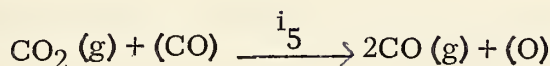
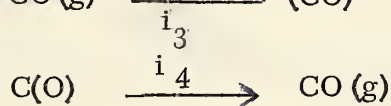
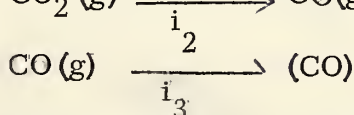
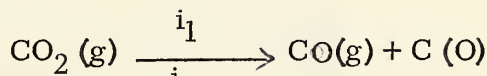
Blackwood and Ingeme (1) gave the final rate equation as

$$R = k_1 \left[\frac{P_{\text{CO}_2}}{1 + k^1 P_{\text{CO}}} \right]^{0.5} \quad k_1 \text{ and } k^1 \text{ being new}$$

constants and showed that it did not fit the experimental results at high pressure. However, the most serious criticism of it is that it again does not allow for the differing reactivities of different carbons unless sites of differing activities are postulated.

Mechanism V

(Blackwood and Ingeme (1))



This is another rather complicated mechanism - the final rate equation after equating the balance of the absorbed species is

$$R = \frac{k_1 P_{CO_2} + k_4 P_{CO} P_{CO_2} + k_5 P_{CO_2}^2 - k_8 P_{CO}^2}{1 + k_2 P_{CO} + k_3 P_{CO_2} + k_6 P_{CO} P_{CO_2} + k_7 P_{CO_2}}$$

where k_{1-8} are constants and functions of the rate constants for the individual reactions. This reduces to

$$R = \frac{k_1 P_{CO_2} + k_5 P_{CO_2}^2}{1 + k_2 P_{CO} + k_3 P_{CO_2}}$$

for the range of variables studied and fits the experimental facts at high pressures.

Unfortunately, the k 's are too complicated functions of the rate of reactions to test if i_2 / i_3 is a constant.

However, once more, this equation does not explain the difference in rates between different carbons.

Conclusions

The rate of gasification of carbon satisfies an equation of the form

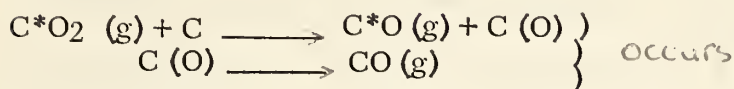
$$R = \frac{K_1 P_{CO_2}}{1 + K_2 P_{CO} + K_3 P_{CO_2}}$$

The values of K_1 , K_2 , K_3 (and K_4) are dependent apparently on the nature of the carbon and none of the mechanisms allows for this. This is fully confirmed by Walker et al (41) where the values of the different investigators were reviewed, i.e. values of K_1 , K_2 , K_3 , and the overall activation energy, and no agreement was found.

Reconsideration of the experimental evidence shows that:

$\text{CO}_2 (\text{g}) \rightleftharpoons (\text{CO}_2)$ does not occur above 600°C .

$\text{CO} (\text{g}) \rightleftharpoons (\text{CO})$ does occur, but apparently not on the same sites available for CO_2 .



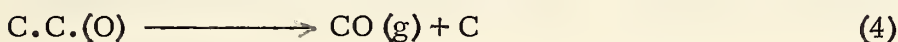
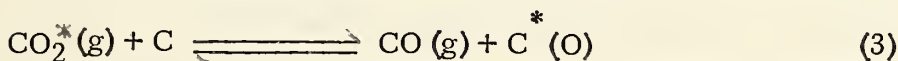
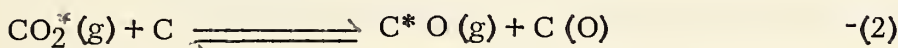
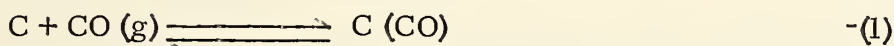
$\text{CO}_2 (\text{g}) + \text{C}(\text{O}) \longrightarrow \text{products}$, does not occur

$\text{CO} (\text{g}) + \text{C} (\text{O}) \longrightarrow \text{CO}_2 (\text{g}) + \text{C}$ occurs

$\text{C}^*\text{O}_2 (\text{g}) + \text{C} \longrightarrow \text{C}^* (\text{O}) + \text{CO} (\text{g})$ occurs to small extent

$\text{C}^* \text{O} (\text{g}) \rightleftharpoons \text{C}^* (\text{O})$ occurs

The scheme of equations resulting is:



If reaction (3) is omitted due to the small incidence of sites on which it occurs and the reverse reaction of (2) does not occur, the resulting scheme of equations is the same as that for Mechanism I. If the reverse of reaction (2) does occur, the scheme of equations reduces to that of Mechanism II for a flow system, once the carbon monoxide adsorption has reached equilibrium. Superficially, then, either Mechanism I or II is suitable with Mechanism II appearing more probable. The objections raised earlier may consequently be directed at the assumptions in these mechanisms, i.e., that of equivalent sites and the removal of one carbon atom causing one new site. If either of these two restrictions are raised, the variation found in the rate constants may readily be

explained. Physically speaking, the reaction can be visualized as taking place on different kinds of sites, e.g., the carbon atoms bonded in different manners to the matrix and hence a spectrum of activities would be expected. The rate of decomposition of the oxide would then be expected to vary with the different sites, each site would not necessarily evolve one new site and if a group of carbon atoms formed a site, the carbon atom leaving the surface due to the decomposition of oxide might not be that which was most closely associated with the oxygen on its removal from carbon dioxide.

The Influence of the Solid Phase on the Reaction Rate

The preceding discussion has pointed out the failure of the mechanisms assuming equivalent sites, to explain the differences in reactivities of different carbons as exemplified by the "constants" K_1 , K_2 , K_3 in the rate equation

$$R = \frac{K_1 P_{CO_2}}{1 + K_2 P_{CO} + K_3 P_{CO_2}}$$

It therefore becomes necessary to take a closer look at the solid carbon and its influence on the reaction rate. In order to do this, it is first necessary to consider a model for the charcoal.

The Structure of Active Charcoal

The pore structure of a charcoal may be divided into three systems, a micropore system of dimensions of the order of 10^{-7} cm.,

a transitional system intermediate between the micro and macro pore systems and a macropore system of dimensions of the order of $1\ \mu$.

Leont'ev and Lukyanovich (23) used an electron microscope to study carbon particles by the replica method and found the transitional pores to be a series of connected spherical cavities due possibly to gas bubbles forming during carbonization and then coalescing by breaking the common wall. The macropores were found to be cracks which were ascribed to shrinkage or channelling to allow for escaping gases during the manufacture. The micropores were too small to be measured by this method but their dimensions are such that they may be envisaged as the gaps and crevices due to the irregular stacking of the individual lamellae of which the carbon is composed.

It will be assumed that the micropore system leads from the external surface and the larger pores. The large area due to these micropores may readily be shown using standard nitrogen adsorption techniques (see Section IV 8) and their size range may be illustrated by adsorption experiments using gas molecules of different kinds. This kind of experiment, e.g. Walker et al (37), has shown that the smaller molecules of gas give larger surface areas and in fact a pore size distribution curve may be obtained.

The individual lamellae may be considered to be graphitic

like in structure* with peripheral hydrocarbon shells and the remaining functional groups bonded at the crystal edges. Some of these lamellae will be bonded to mineral matter, e.g. components of the ash, and this may affect their reactivity. There will also be a certain amount of ash present not bonded to the crystallites.

Factors Affecting the Reactivity of Charcoal

With a model for the charcoal now in mind, the factors which affect its reactivity will be discussed. They will be classified into two types.

Type I

Factors descriptive of the charcoal

1. Crystallite factors

- (a) number and size
- (b) orientation (especially ratio of basal plane to edges in the surface).
- (c) presence of defects
- (d) thermal conductivity

2. Impurities

- (a) impurity content
- (b) uniformity of impurity distribution in the carbon matrix
- (c) nature of the impurities and their chemical form in the carbon.

*Footnote

The assumption of graphite like lamellae was questioned by S. Ergun (12) who found that small tetrahedral (diamond like) structures yielded X-ray patterns overlapping those of graphite like layers and also felt that the hardness and non-graphitizability of some amorphous carbons supported the view that the X-ray interpretation was inconclusive. However, in view of the aromatization of the components during the carbonization process, the prevailing view of graphitic like lamellae will be adhered to.

Type II

Factors which modify the Type I factors

1. Heat treatment
2. Irradiation

The Type I factors will now be considered in turn, together with the effect of heat treatment and irradiation upon them. During the discussion of these factors, evidence will be presented for at least two kinds of active site and a summary of this is given below.

Evidence for at least two kinds of active site

- (a) The existence of two kinds of graphite crystal whose reactivity depends on heat treatment and irradiation.
- (b) The reactivity of the edge atoms of the carbon crystallites coupled with the surface oxide coverage of the complete crystallite.
- (c) The existence of two types of E.S.R. signal, one showing line broadening on the admission of oxygen and the other found in higher temperature carbons not exhibiting line broadening.
- (d) The fact that about 50 oxygen atoms were chemisorbed in one particular sample to remove one electron spin.
- (e) The existence of both "acidic" and "basic" carbons.

Crystallite Factors

These factors are not independent and consequently their interrelation precludes a complete separation into the topics listed. A convenient starting point is the reactivity of single pure graphite

crystals because of the analogy between these and the quasi-graphitic parallel layer groups, which are the constituents of the model of charcoal assumed.

Hennig (19) found two classes of graphite crystals differing in reactivity, believed due to the presence in only one case of excess lattice vacancies, possibly initially present or introduced during heating (it is known that a certain number of defects in a crystal may give a thermodynamically more stable system than the defect free crystal, e.g. the alkali halides). Lattice defects produced by neutron irradiation changed the kinetics of the surface reaction, e.g. in one case, the activation energy was reduced from 78 k cal. to 48 k cal per mole by an irradiation of about $nvt = 10^{20}$. This evidence may be interpreted as showing the existence of at least two kinds of active carbon sites, one of which is associated with the lattice edges and one with the lattice vacancies. Other evidence supporting this view may be derived from several sources. For example, Boehm et al (2), found that when a carbon was out - gassed at 1000°C and then brought into contact with oxygen at room temperature, it was covered with basic oxides (determined by neutralization with HCl. soln.) but when carbon reacted with oxygen at 400-500°C, acid surface oxides were formed of variable acidity (determined by neutralization with alcoholic KOH or aq. NaOH soln.) and not all of the acid groups in the graphitic oxide carbon black could be located at the edges of carbon layers. Consequently, some of the oxide being formed in the planes of the lamellae

provides a satisfactory explanation. Similarly, the experimental results of Hennig (19), may be explained, where degassing a single graphite crystal after an experiment yielded enough carbon monoxide and dioxide to have covered the whole surface. Transmission electron micrographs ruled out the possibility of a sub-microscopic roughness of the crystal edges causing a ten-fold increased area, but of course the possibility of the surface oxide being a multilayer on the edge atoms remained. Harker et al (18) found for a particular sample that about 50 oxygen atoms had to be chemisorbed to remove one electron spin. There is, therefore, evidence of enough oxide to cover the whole surface of which only a small proportion affects the E.S.R. signal of the oxygen free carbon. The widely varying surface coverages found by other investigators, e.g.

Reif (28) 75% coverage by CO on a degassed high temperature coke;

Gadsby et al (15) 0.5% coverage during reaction with CO₂ on a coconut char;

Vastola and Walker (36) 1.5% coverage using oxygen on graphon; may partially be explained by chemisorption of carbon monoxide on the surface which does not take part in the reaction, as deduced earlier.

There is also a hysteresis effect in the reactivity of carbon to carbon dioxide, oxygen and steam as shown by Boulangier et al (4), even around the maximum reactivity found at 1550°K for the particular sample studied. This may be due to a time lag for thermal annealing, i.e. surface migration of a site to a more stable place in the lattice or

time to allow the equilibrium number of vacancies to develop. Consequently, the initial rate of reaction at a new temperature, after a sudden temperature change, initially resembled the rate at the previous temperature until the new equilibrium was reached.

A subsidiary effect reported by Hennig (19) was that the oxidation steps in different directions on a graphite crystal gradually assumed a crystallographic orientation. This was explained by the incidence of three types of boundary atoms in a graphite layer causing slightly different reactivities in the different directions. A much more important directional effect and one which was more or less assumed earlier is the location of active carbon atoms on the crystallite edges. This has been demonstrated clearly by both Hennig (19) and Smith and Polley (33). Hennig (19) found that the number of active carbon atoms was of the same order as the number of edge atoms and ten times less than the number of basal carbon atoms in the surface.

Smith and Polley (33) found that during the oxidation of a fine thermal carbon black, the surface area increased six-fold due to the development of porosity, whereas a similar graphitized sample was much less reactive and the slight area decrease was related to the decrease in particle size. The X-ray diffraction data revealed a five-fold increase in the size of the parallel groups in the latter case and hence the surface appeared to be more uniform. The interpretation was that the oxidation occurred by preferential attack at the high energy sites on the carbon surface. If these were mainly the edge atoms of the

crystallites, one would expect preferential stripping off of layers in the case of the more highly ordered graphitic carbon and the development of a certain amount of internal porosity due to reaction along the crystallite edges eating into the less highly ordered carbon black.

Consequently, it would be expected that the fraction of the carbon surface exposing crystallite basal planes will markedly affect the subsequent gas reactivity and this has been confirmed by Walker and Rusinko (40) who used x-ray data to show that a higher percentage of basal planes in the surface of a coke particle resulted in a lower reactivity.

Some E.S.R. evidence which is pertinent to the present discussion will now be considered. It may be possible to correlate the active sites associated with the lattice edges and vacancies with the two kinds of E.S.R. signal found by Collins et al (7). The first kind of unpaired electron gave a signal which showed considerable line broadening when oxygen was admitted and was found only in carbon not heat treated above a certain temperature (1400°C in this case), which was the temperature of maximum reactivity, a characteristic temperature for each carbon. This type of signal was associated with unpaired mobile π electrons stabilized by resonance energy in large condensed ring structures many of which probably contained oxygen. Above 1400°C, the first kind disappeared and a new species appeared which gave a line exhibiting no broadening

when oxygen was introduced. This line was ascribed to localized electrons at defects in the graphitizing lattice. Harker et al (18) found that the E.S.R. signal not exhibiting line broadening with oxygen was found to decrease on reaction. This was explained as due to oxide formation, a chemisorption process requiring a high activation energy because it occurred slowly both at room temperature and 500°C, although faster at the higher temperature.

To summarize the E.S.R. evidence, it can be said that although the interpretation is not completely clear, two different kinds of signals are observed and thus two different sources for these signals may be deduced. Finally, the thermal conductivity of the material may have an effect due to thermal considerations at a site between reaction encounters with gas molecules.

Impurities

Amongst the impurities, one might possibly include hydrogen and oxygen. The effect of surface oxides has already been mentioned. Grisdale (16) found that in the pyrolysis of methane, the extent of preferential crystallite orientation in the carbon formed, systematically depended on the conditions and it has already been shown that this will affect the subsequent reactivity. It was suggested by the authors that hydrogen influenced the deposition only in its effect on the rigidity of the platelets in the condensing drops and hence the orientation of the carbon deposited. A similar reasoning might be applied to the effect of hydrogen in charcoal. The effect of functional

groups on the reactivity does not seem to be understood; they possibly have both a steric effect as above and play a part in the reaction.

The inorganic impurities in the carbon may or may not have an effect on the reactivity. The reaction rate increases on the introduction of iron and potassium, Semechkova and Frank Kamenetzky (31). Vastola and Walker (36) also reported catalysis by iron. However, no correlation between ash content and reactivity was found by Walker and Rusinko, (40) and Boehm et al (2), although the latter found a marked difference in reactivity on heat treatment. A series of carbons produced from coal tar pitches were, in the majority found to increase in reactivity on graphitization despite a decrease in the surface area and impurity content, and an increase in crystallite size. This increased reactivity was explained by postulating that the metallic impurities in close association with a carbon matrix could affect the distribution of electrons by accepting an electron or by forming a covalent bond. Heat treatment allowed this interaction by solid state diffusion of the impurities along the boundaries of the carbon crystallites and also caused the crystallites to grow, increasingly at higher temperatures, thus allowing a given impurity atom to catalyze more carbon atoms because of the good electron transfer properties across the basal planes of the crystallites. The lattice defects also have an effect here. Henning (19) found that the lattice defects caused the formation of pits in the layer planes

of graphite during oxidation and this facilitated the penetration of any catalytic matter present into the crystal. In defect free crystals, the catalyst was characteristically found in channels.

Summary

Reaction occurs on the individual lamellae of which the carbon is composed possibly hindered by a diffusion resistance due to the extensive pore system in the material. Attack occurs primarily at the edges of the crystallites and at lattice defects in them and consequently the reactivity will depend upon the crystallite factors already listed. The mechanism of catalysis by inorganic material of this reaction is at present unpredictable.

III. EXPERIMENTAL APPROACH

As shown in Section II, the reaction $C + CO_2 = 2CO$ proceeds by a complex mechanism involving probably more than one type of active site, thermal annealing, and catalytic effects due to foreign matter. An absolute determination of a general mechanism for so heterogeneous a substance as coconut charcoal is therefore impossible and a somewhat empirical experimental approach has accordingly been adopted.

This involved oxidizing a series of coconut charcoals by carbon dioxide at between 850°C and 1000°C and relating their reactivities to other properties of the carbon. The reactivities were defined in terms of the three rate constants contained in the general rate equation.

IV. DESCRIPTION OF CHARCOALS

1. Source and Preparation

The series of steam activated coconut shell charcoals were supplied by Barneby-Cheney and although activated similarly came from different batches. They were prepared by charring coconut shells and then reacting them with steam at a temperature of about 600°C to activate them which increased their surface area by etching out the pores. The charcoals were screened and the 10-12 mesh size fraction retained.

One of the series, #3a, was ground in a ball mill and two finer fractions, #3b and #3c, were collected.

2. Carbon, Hydrogen and Ash Determinations

Carbon and hydrogen were determined by burning a sample of charcoal in oxygen and absorbing and then weighing the carbon dioxide and water evolved. The weight of the residue gave the ash.

Results

TABLE 3

Sample No.	C	Dry Basis H	Ash	Dry Ash Free Basis C	Dry Ash Free Basis H
1	84.49	2.47	0.73	85.1	2.49
2	92.42	.60	2.07	94.5	.61
3a	N.D.	N.D.	3.96		
	N.D.	N.D.	.02		
	N.D.	N.D.	3.12		
	N.D.	N.D.	3.32		
	N.D.	N.D.	8.77		
	96.08	.74	.44	96.50	.74
3b	91.43	.64	5.24	96.48	.68
3c	92.30	.70	4.48	96.62	.73
4	95.71	.64	.24	96.0	.64

A variation in sampling can be clearly seen. However, the sample size for the ash determinations was comparable with the charge used for the kinetic experiments. As the fluctuations in the reactivity of various

samples of #3a were much smaller than the difference in reactivity between #3a and #3b charcoal, whereas the fluctuations in ash content were comparable, the variation in reactivity could not be more than slightly dependent on the ash content.

3. Total Acidity and Carboxyl Groups

Wood and Warchola (44) made the following determinations:

The total acidity was determined by adding barium hydroxide solution to the crushed sample and titrating a portion of the resulting solution with dilute hydrochloric acid.

The carboxyl groups were determined by adding sodium acetate and acetic acid to the sample and titrating a portion of the resulting solution with dilute NaOH solution.

The results are tabulated below:

TABLE 4

Sample No.	Total Acidity milliequivalents/gm.		Carboxyl Groups milliequivalents/gm.	
1	4.57		-0.75	
2	1.33		-3.81	
3a	0.82	0.92	-0.42	-0.37
3b	0.82	0.82	-0.37	-0.37
3c	0.92	0.92	-0.43	-0.43
4	2.17		-6.18	

The variation between samples 3a-3c is less than the experimental error.

The surface is apparently basic, a common feature of this kind of active char, possibly due to the presence of polycondensed aromatic hydrocarbons which preferentially adsorb hydrogen ions.

4. Size, Activity, Appearance and Density

The sample numbers, mesh sizes, and available data (17) are tabulated below:

TABLE 5

Sample No.	Mesh Size	Nominal Activity	Actual Activity	Helium [‡] Density gm/cc	Apparent cc.chloropicrin Density gm/cc	adsorbed/gm
1	10~ 12	0	--	1.559	--	--
2	10~ 12	10	9.5	--	0.600	10.1
3a	10~ 12	60	64.4	2.110	0.513	80.6
3b	48~ 65	60	--	--	--	--
3c	100~150	60	--	--	--	--
4	10~ 12	90	89.6	--	0.384	14.9

Here, the activity of a charcoal is defined as the time in minutes to break through, for the accelerated chloropicrin test in a standard procedure*. The activities converted to a weight basis using the densities given by the manufacturer and expressed as average concentrations[†] at break through are reported

* Air, containing 0.286 moles chloropicrin per litre, was passed through a 10 cm. column at a rate of 1 litre per min. per cm., until chloropicrin was detected in the exit stream.

† cc. at S.T.P. assuming ideal gas behaviour per gm.

‡ Helium density is the density of the solid material of the carbon particles, so called due to the method for determining the volume.

in the last column. The size of the chloropicrin molecule and the nature of the test give a value for the activity indicative of the readily available internal surface of the particles. The samples were also examined under a microscope with the 10-12 mesh particles being magnified 500 and the finer particles 1,000 times. The surface roughness order was as follows: 1 and 3c > 3b > 2 = 3a > 4, as well as could be determined by the eye. The photographs on pages 33 and 34 illustrate this point.

5. Infrared Spectra

Pellets made with potassium bromide and examined in the usual manner showed no structure in the infrared, i.e. all had a low general background absorption with no diagnostic features.

6. Electron Spin Resonance

Due to the ready availability of the apparatus, the E.S.R. signals of a number of samples of the charcoal were examined in the X-band region. Marked differences were recorded both in the intensity and nature of the signals. No interpretation has been attempted here but the different signals, obtained by Elofson (9), together with his comments are tabulated on page 35.

EDGES OF CHARCOAL PARTICLES
(Nominal Activity 60) (x395)



Charcoal No.3a 10-12 Mesh



Charcoal No.3b 48-65 Mesh



Charcoal No.3c 100-150 Mesh

EDGES OF CHARCOAL PARTICLES (x395)



Charcoal No.1 Activity 0



Charcoal No.2 Activity 10



Charcoal No.3a Activity 60



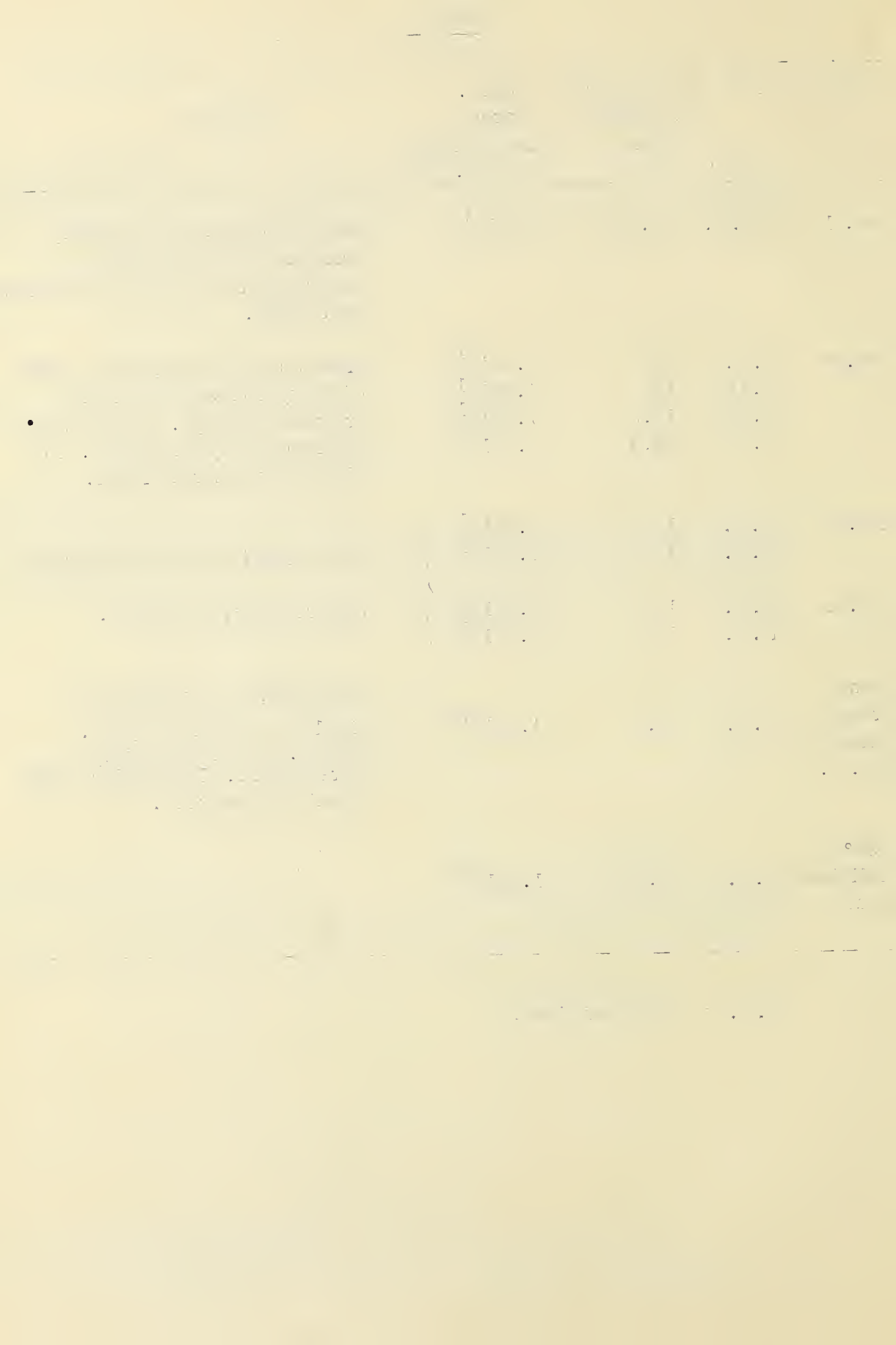
Charcoal No.4 Activity 90

Figure 2.

TABLE 6

Sample	Ash	Peak to Peak Line Width gauss	Concn. in Vacuo free radicals/ gm.	Remarks
No. 1	N.D.	0.84	8×10^{19}	Strong resonance in air greatly narrowed and intensified on evacuation resembling the cellulose char below.
No.3a	N.D.	33	1.0×10^{18}	Broad asymmetric signal in vacuo of the type observed in chars prepared at temps. of about 750°C and reported by Mrozowski. No signal was observed in air.
	3.12	15	1.2×10^{19}	
	3.32	16.5	7.9×10^{18}	
	8.77	20.0	3.6×10^{18}	
No.3b	N.D.	14	5.0×10^{18})	Weak signal in air and moderately intense signal in vacuum.
	N.D.	14	5.0×10^{18})	
			)	
No.3c	N.D.	13	6.2×10^{18})	
	N.D.	13	6.2×10^{18})	
Dust from grinding No. 3.	N.D.	13.5	1.6×10^{19}	The signal in a vacuum was similar to that given by No. 2 and No. 3 but considerably more intense. In air only a weak signal was produced.
650° C cellulose char	N.D.	0.84	1.0×10^{20}	

N.D. = not determined.



7. Porosimetry

Pore volume distribution measurements were carried out by G.T.Shaw, B.I.Parsons and W.K.Merrill at the Fuels and Mining Practice Division, Dept. of Mines and Technical Surveys, Ottawa, using the high pressure mercury porosimeter technique developed by Ritter and Drake (30). The results, which in general had good reproducibility, showed that the volume of pores in the 200 to 20 $\overset{\circ}{\text{\AA}}$ range was much less in the case of the samples Nos. 3b and 3c than in the case of No. 3a, even after a 12% by weight burnoff.

The distribution function D is defined by

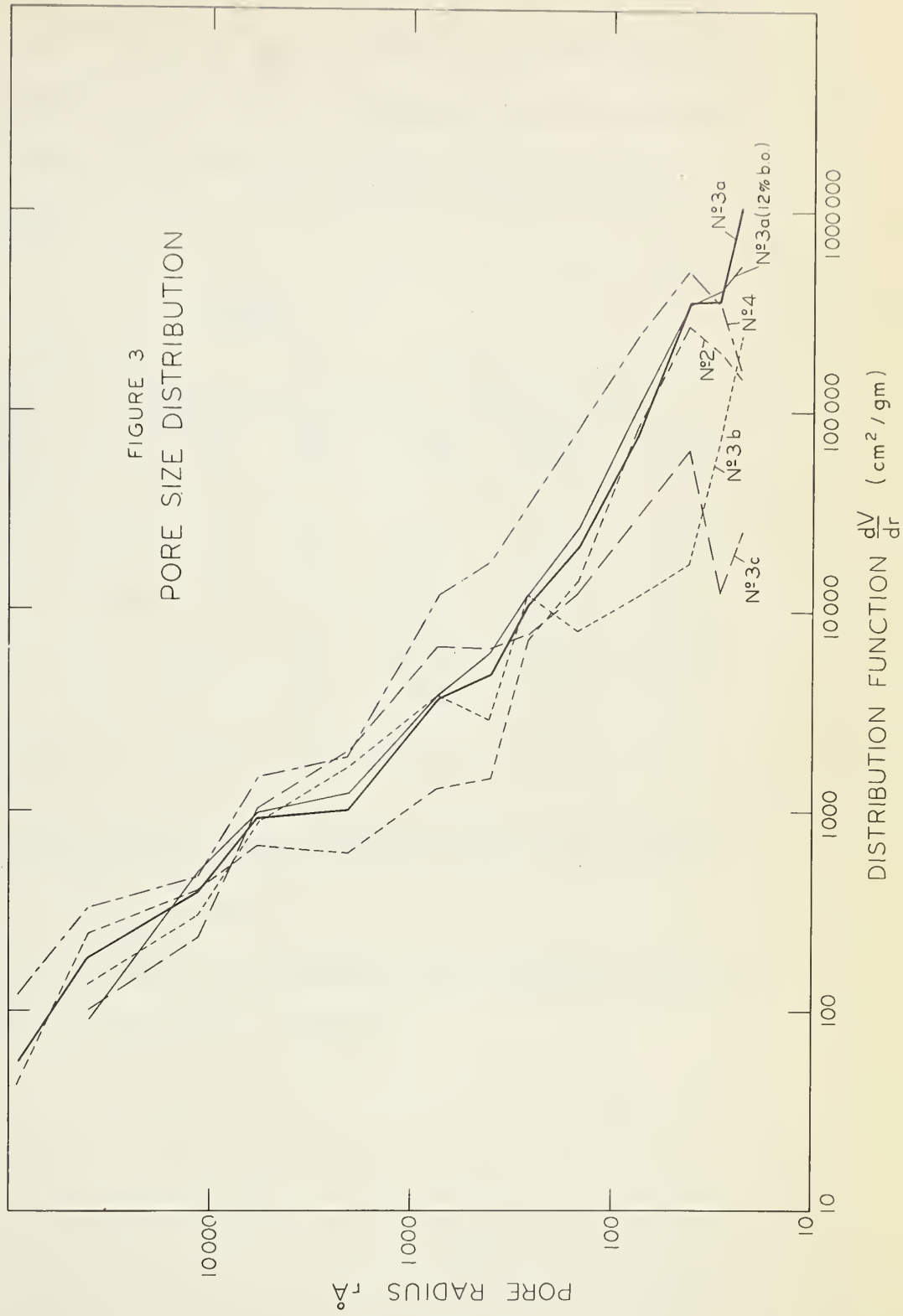
$$D = \frac{dV}{dr}$$

where V = cumulative volume per gram charcoal of mercury in the pores.

r = radius of the pores ($\overset{\circ}{\text{\AA}}$).

The distribution function is plotted against the pore radius in Fig. 3 to illustrate the pore size distribution.

It can be seen that there is a steady increase in pore volume with decreasing pore radius with the trend of the graphs indicating that a large portion of the surface area is contained in pores smaller than 20 $\overset{\circ}{\text{\AA}}$ radius. This finding is in agreement with the work of Morrison and Miller (25) who obtained a mean radius of 11 $\overset{\circ}{\text{\AA}}$ for a similar series of charcoals by comparing the adsorption of various organic acid adsorbates. The nitrogen adsorption experiments IV. 8 support this view.



8. Sorption Properties

Reaction takes place at active centres at which initial physical adsorption might also be expected. Accordingly, the isosteric heats of adsorption of nitrogen at low surface coverage, (together with the nitrogen monolayer values at 77°K) obtained by Haggood and Hanlan (17) are tabulated below.

TABLE 7

Sample No.	Nitrogen Monolayer cc./gm.	Initial Heat of Adsorption					Kcal/mole of i C ₄ H ₁₀
		CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	
1	200	5.3	7.8	8.0	10.6	11.8	13.5
2	210	5.2	7.6	7.9	10.3	11.3	12.6
3	367	4.7	7.0	7.4	9.3	9.7	11.8
4	631	4.1	6.4	6.6	8.4	8.8	11.1

N.B. The initial isosteric heats of adsorption varied with the degree of activation over a range of around 25%

Taking the initial heat of adsorption of No. 4 charcoal as unity for each adsorbate, these data may be retabulated:

TABLE 8

Sample No.	Heat of Adsorption relative to No. 4 Charcoal						average
	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	iC ₄ H ₁₀	
1	1.29	1.22	1.21	1.26	1.34	1.22	1.26
2	1.27	1.19	1.20	1.23	1.28	1.14	1.22
3	1.15	1.09	1.12	1.11	1.10	1.06	1.10
4	1.00	1.00	1.00	1.00	1.00	1.00	1.00

The fractional surface area taking part in the reaction has already been discussed in the Literature Review. In order to see if there is any correlation between surface area and reactivity and also to look at the change in surface area with burnoff, adsorption experiments were carried out using liquid nitrogen and the standard technique. Various modes of interpretation were tried; that of Cranston and Inkley (8) required more accurate measurements than were available and the methods of Brunauer - Emmett - Teller (10) and Harkins and Jura (10) gave curved plots where straight ones were predicted. The Langmuir isotherm was found to yield straight lines in accordance with the theory and consequently was used for characterization. The working formula is

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{KV_m}$$

where P = pressure of adsorbate

V = volume of adsorbate

V_m = volume of adsorbate for a complete monolayer

K = a constant

and P_0 = S.V.P. of adsorbate at temperature of experiment.

The slope of the plot of $\frac{P}{V}$ against p yields V_m . In this case

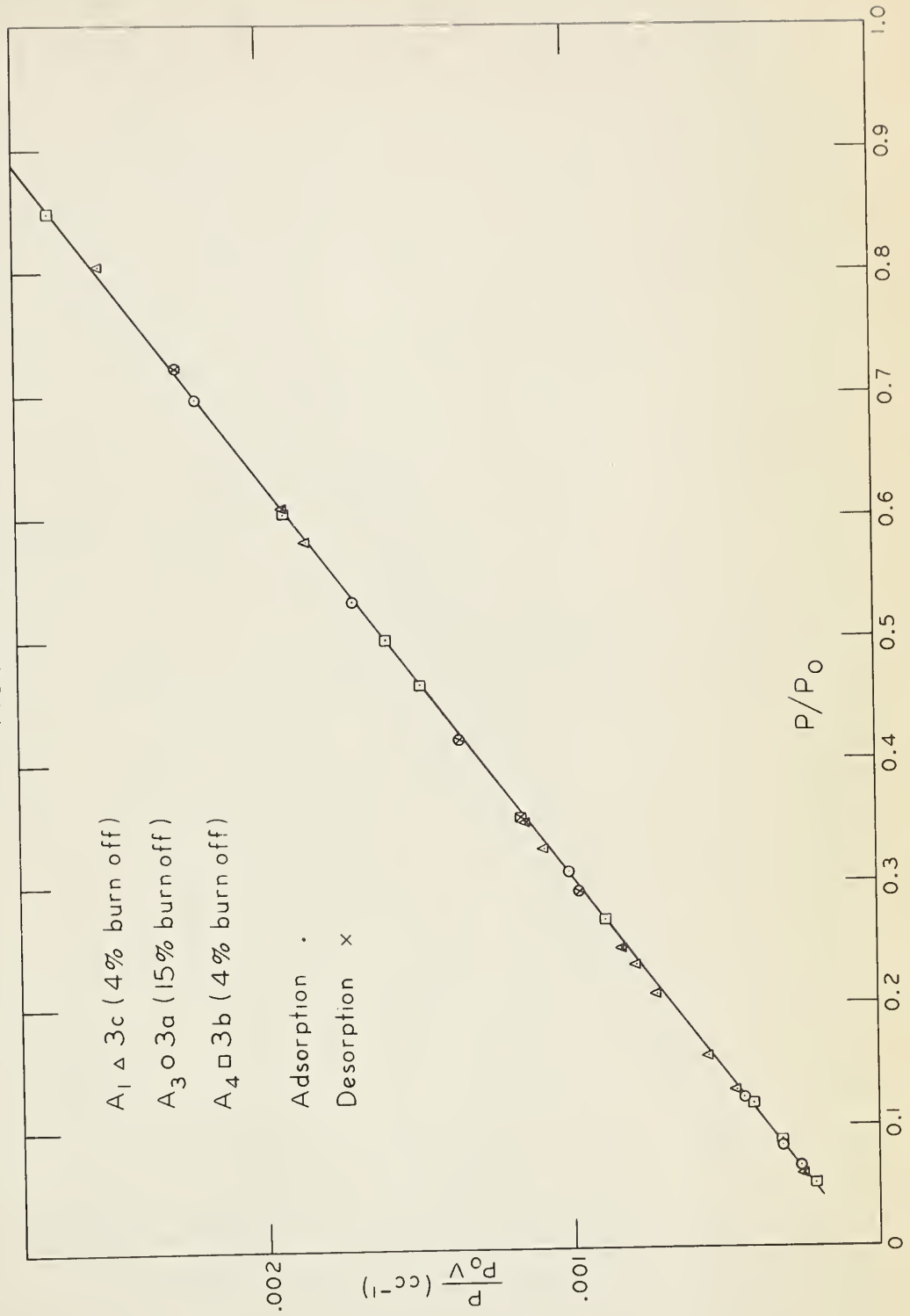
$\frac{P}{P_0 V}$ was plotted against $\frac{P}{P_0}$ in order to eliminate the slight variations

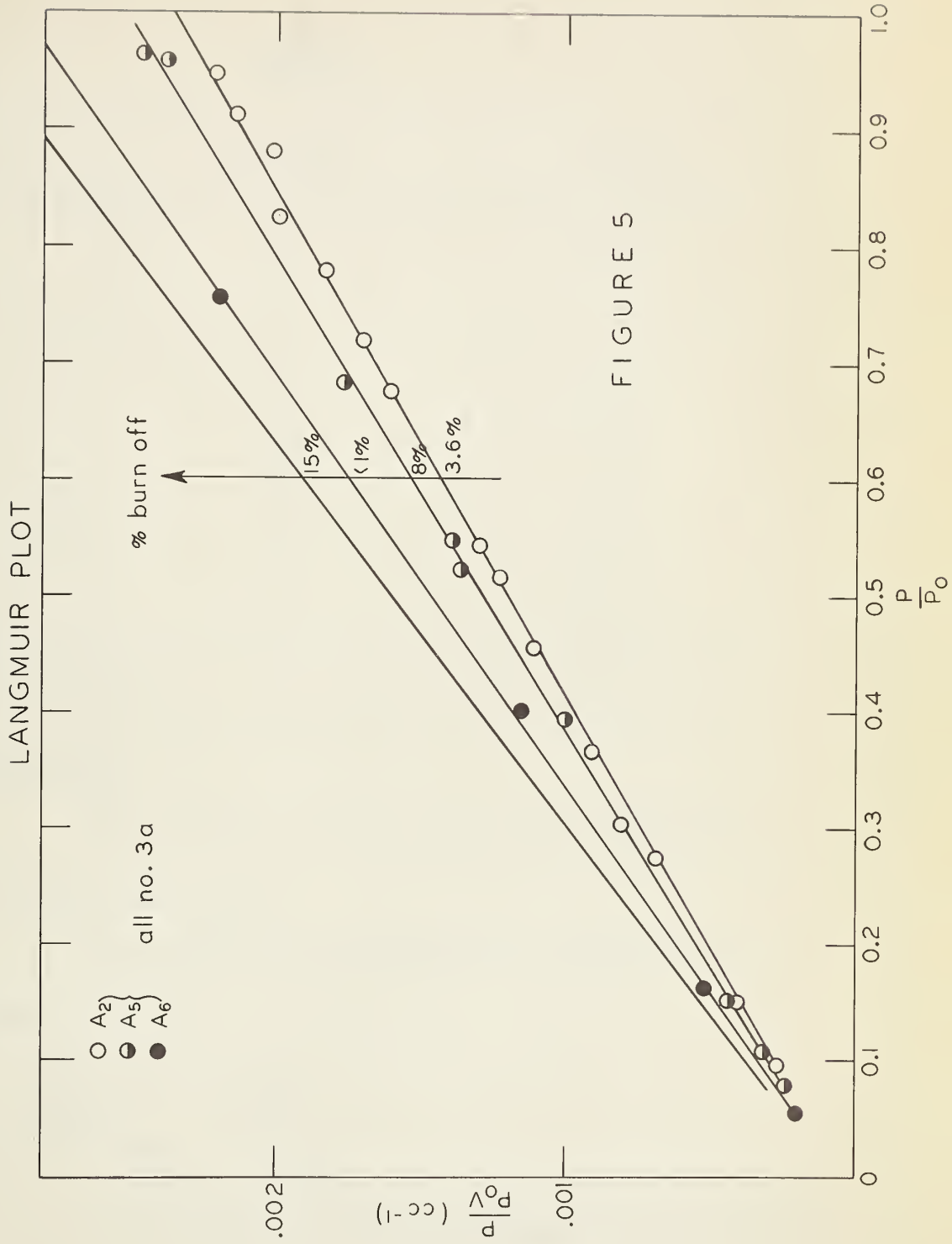
in temperature of the batches of liquid air used in the different experiments.

The results are depicted graphically in the form of Langmuir plots, pages

41 and 42.

LANGMUIR PLOT
FIGURE 4





Conclusions

The resulting nitrogen monolayer values are tabulated below:

TABLE 9

Sample No.	Burnoff %	cc./gm.
3a	4	430
3b	4	325
3c	4	325
3a	<1	350
3a	3.6	430
3a	8	400
3a	15	325

cf. the value of 367 cc./gm. given in (17) for the charcoal from which these were derived.

The variation in nitrogen monolayer value with burnoff is illustrated graphically in Fig. 6.

At $P = P_0$ the pores presumably will be filled with a condensed phase of nitrogen

$$\left(\frac{P}{P_0 V} \right)_{P=P_0} = \left(\frac{1}{V} \right)_{P=P_0}$$

If it is assumed that this condensed phase has the same density as that of liquid nitrogen*, the actual pore volume per gram may be readily

* The adsorbed molecules in the pores are probably compressed.

VARIATION IN NITROGEN MONOLAYER VALUE WITH BURNOFF

3a Charcoal

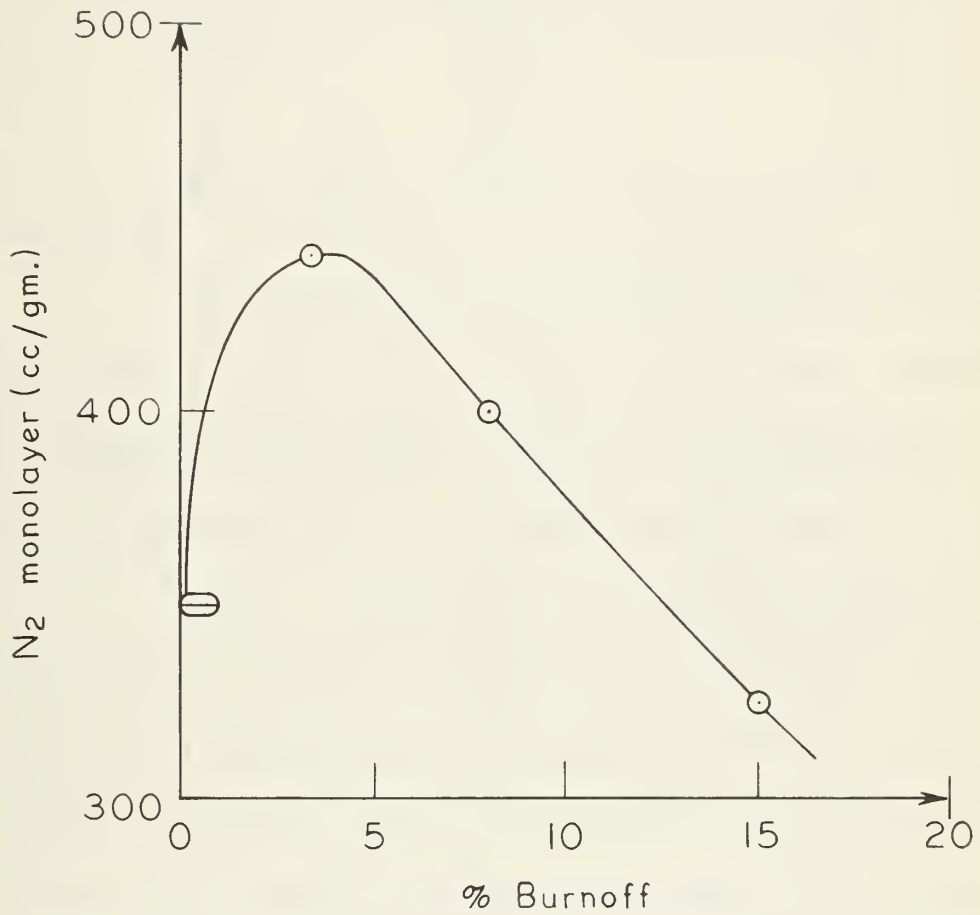


FIGURE 6

calculated. These values are tabulated below with the porosimeter values obtained at 50,000 p.s.i.a.

TABLE 10

Sample No.	Pore Volume ml./gm.	Porosimeter volume at 50,000 psia ml./gm.	% pores filled by mercury
3a	.660	0.391	59
3b	.497	0.187	38
3c	.497	0.208	42

The last column of the table represents either the percent surface area found in pores with radius greater than $20 \text{ \AA}$, a factor reflecting the compression of liquid nitrogen in the pores, a factor reflecting the presence of bottleneck pores*, or a combination of these effects.

Table 9 shows that No. 3a charcoal has a greater surface area than Nos. 3b and 3c and therefore is a different material. Fig. 6 shows the initial increase and then the decrease in area of No. 3a charcoal with burnoff, agreeing with Walker and Raats (39) according to whom, the pore area of a char possessing a similar nitrogen isotherm was also found to increase to a maximum. The maximum in their case was found at 23% burnoff compared with 4% here and was paralleled by the change in specific reaction rate per unit pore volume. They also found no trend between gasification temperature and increase in pore volume, the average pore

* Bottleneck pores cause a low mercury porosimeter reading.

(7) —

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radius decreased markedly on reaction and that the sum of the pore volumes calculated from the micropore (nitrogen adsorption) and macropore (mercury porosimeter) distributions was less than that calculated from density (helium and mercury) data. Thus the initial increase in area may be due to the opening up of some of the initially non-connected transitional pores and their accompanying micropore structures.

9. Reactivities of the Charcoals

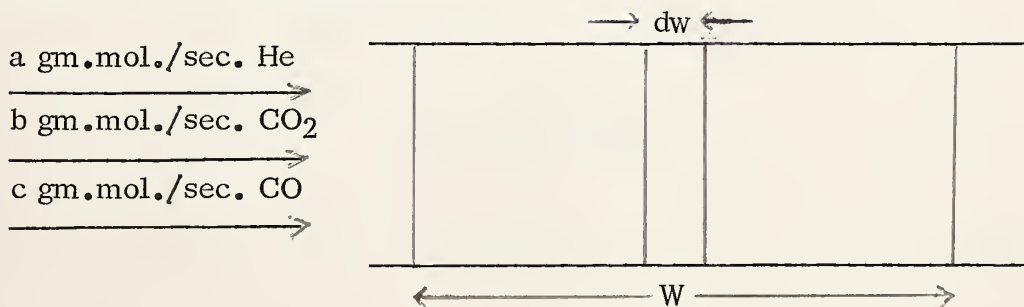
Introduction

The rate of reaction is expressed by:

$$R = \frac{K_1 P_{CO_2}}{1 + K_2 P_{CO} + K_3 P_{CO_2}}$$

According to Wicke (43), the terms in the denominator are of strong influence at relatively low reaction temperatures with the order of reaction becoming zero at the higher ones. Brown (6) found a zero order reaction at carbon dioxide partial pressures above 3 cm. of mercury and in the discussion following (43) Walker stated having found a zero order reaction for petroleum coke at partial pressures of carbon dioxide ranging from 1/5 to 1 at. at a temperature of 1100°C. The decomposition and desorption of the surface oxide complex would be expected to be the rate controlling step under zero order conditions and so the experimental range was chosen to be near the above in order to see the surface influence most clearly. This did not result in zero order kinetics.

Theory of the Flow Reactor



Consider an elemental disc containing dW gm. mols. of charcoal
in a cylindrical bed containing W gm. mols. of charcoal.

Let the bed inlet flow rates be:

$$\begin{array}{llll} a & \text{gm. mol./sec. He} \\ b & \text{" " " CO}_2 \\ c & \text{" " " CO} \end{array}$$

The constant helium flow rate will be used as the gas phase reference.

Let x be the conversion of carbon dioxide at the beginning of the
differential element measured in gm. mol. CO_2 converted per gm.
mol. He.

Let R be the rate of conversion in the differential element measured
in gm. mol. C gasified per gm. mol. C per sec.

Assuming that 1 gm. mol. CO_2 gives 2 gm. mol. CO, the composition
of the gas entering the element will be:

$$\begin{array}{ll} a & \text{gm. mol./sec. He} \\ (b-ax) & \text{gm. mol./sec. CO}_2 \\ (c+2ax) & \text{gm. mol./sec. CO} \end{array}$$

A carbon balance on the element gives:

$$adx = RdW \quad (1)$$

$$\text{where } R = \frac{K_1 P_{\text{CO}_2}}{1 + K_2 P_{\text{CO}} + K_3 P_{\text{CO}_2}} \quad (2)$$

$$\text{and } P_{\text{CO}} = \frac{c + 2ax}{a + b + c + ax} \quad (3)$$

$$P_{\text{CO}_2} = \frac{b - ax}{a + b + c + ax} \quad (4)$$

(1), (2), (3) and (4) are combined and integrated

$$\frac{1}{a} \int_0^W dW = \int_0^{x_0} \left\{ \frac{K_3}{K_1} + \frac{(2K_2 + 1) ax}{(b - ax) K_1} + \frac{a + b + c + K_2 C}{(b - ax) K_1} \right\} dx$$

where x_0 is the conversion of carbon dioxide at the outlet of the bed

$$\therefore \left[\frac{WK_1}{ax_0} + 1 + \left(\frac{a + 2b + c}{ax_0} \right) \ln \left(\frac{1 - \frac{ax_0}{b}}{1} \right) \right] = K_3 - K_2 \left[2 + \frac{(2b + c)}{ax_0} \ln \left(1 - \frac{ax_0}{b} \right) \right] \quad (5)$$

The group ax_0 = gm.mol. CO_2 converted/sec.

K_1 may also be determined using the fact that the

$$\text{equation } R = \frac{K_1 P_{CO_2}}{1 + K_2 P_{CO} + K_3 P_{CO_2}}$$

reduces to $R = K_1 P_{CO_2}$ at very low partial pressures of CO_2

By a similar procedure to the previous one

$$K_1 + \frac{(a + b)}{\left(\frac{W}{b} \right)} \ln \left(\frac{1 - \frac{ax_0}{b}}{1} \right) = \frac{-b}{W} \left\{ \ln \left(\frac{1 - \frac{ax_0}{b}}{1} \right) + \frac{ax_0}{b} \right\}$$

When ax_0 is plotted against b , $\frac{ax_0}{b}$ tends to a limiting value L

given by the slope at the origin and so as b

$$\text{tends to zero} \quad K_1 \rightarrow \frac{-a}{W} \ln (1 - L) \quad (6)$$

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Experimental Apparatus for Flow Experiments

Fig. (7) shows the layout of the flow apparatus. Helium from the cylinder was controlled by a Grove Regulator and, after passing through a length of capillary tube to smooth out flow variations and drying over molecular sieve, could be diverted either through or around the reactor in the furnace by means of the three way stopcock shown. Carbon dioxide from the cylinder also was controlled by a Grove Regulator followed by a capillary tube but was dried using Drierite followed by phosphorus pentoxide (molecular sieves could not be used here since they strongly adsorb carbon dioxide). Carbon monoxide from the cylinder and the carbon dioxide could be introduced into the helium stream as shown.

The Aerograph sampling valve was situated such that the gas flow bypassing the reactor, or flowing through it could be sampled and this was followed up by a soap bubble meter whereby the gas flow rate could be measured.

The apparatus could be evacuated using a Cenco vacuum pump connected to the points shown.

The reactor and connections were made of silica with an axial thermocouple well. Alundum balls filled the lower part of the reactor to provide a bed for the charge - the reactor is illustrated in Fig. (8). The reactor was changed to a 1 cm. I.D. silica tube for Series B and C. The support for the bed was a cylindrical piece of porous refractory brick with a hole bored in the bottom into which

the thermocouple well fitted. The thermocouple used was either Chromel/Alumel or Platinum/Platinum, 10% Rhodium. The furnace used was a cylindrical one with Globar elements and the temperature could be kept reasonably steady throughout a run by using a voltage regulator. The temperature gradient along the bed in Series A was eliminated in the later runs by the introduction of subsidiary heating elements at the ends of the furnace.

Gases used:	CO ₂ bonē dry grade	99.8% pure)
		) Matheson
	CO c.p. grade	99.5% pure)
	He	99.99% pure Airco.

Analytical Apparatus

Analyses were conducted gas chromatographically. The layout is shown in Fig. (9). The cell was a GowMac (pretzel) and the column 6 ft. of 1/4 in. copper tube containing 48-60 mesh silica gel poisoned with 1% glycerine. The column was kept at 100° C using a boiling water bath.

The electrical circuit is also shown in Fig. (10). The helium flow rate used was approx. 1 cc./sec. and the current through the cell was 200 mA. Calibration samples of pure CO₂ and CO were taken before and after each experimental run and their areas, as measured by the Ball and Disk Integrator attached to the Honeywell Recorder used as 100%. The concentrations of component in the samples taken during the experiment were taken directly as the fraction of these areas.

APPARATUS FOR FLOW EXPERIMENTS

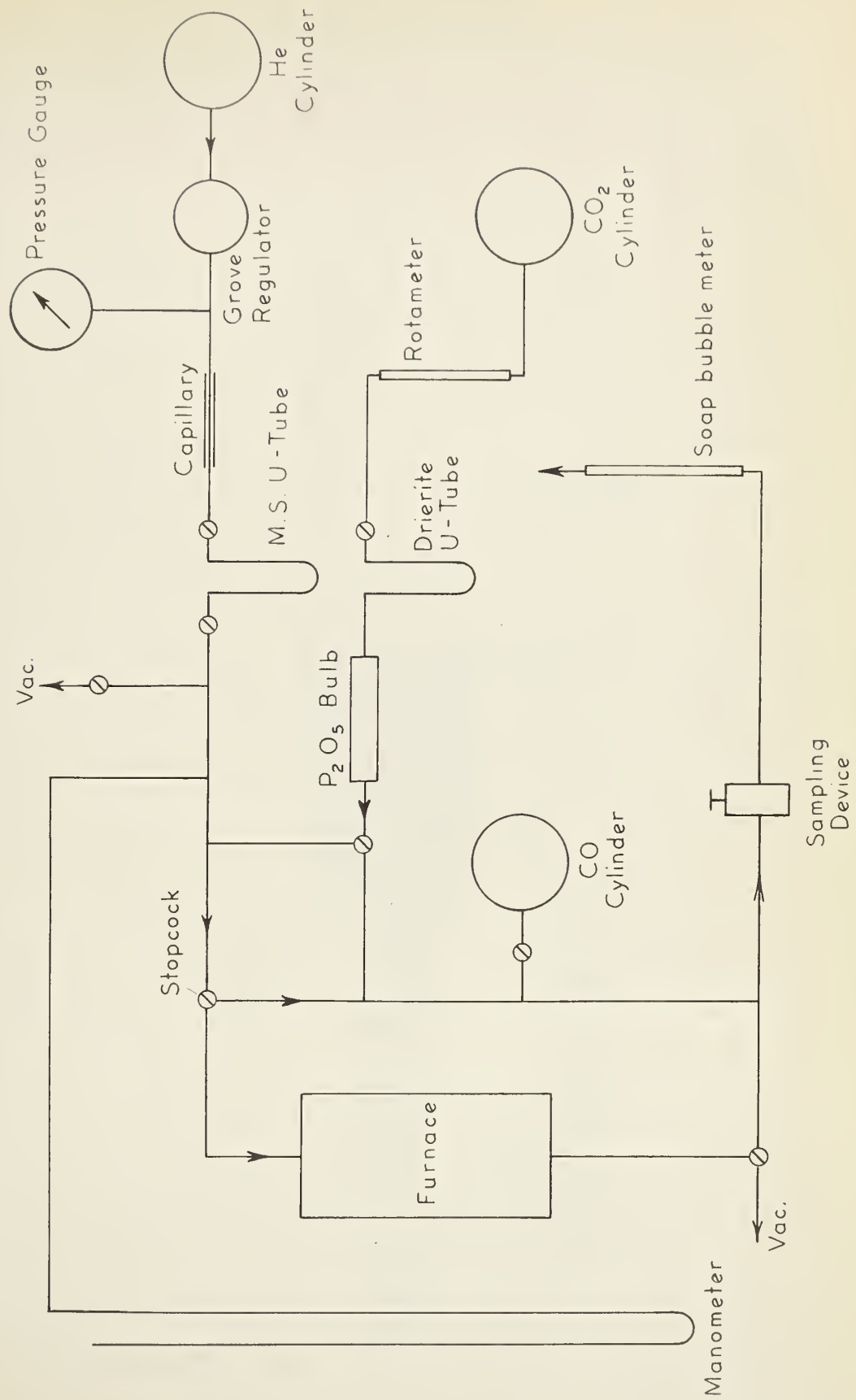


FIGURE 7

REACTOR

Scale: Full Size (approx.)

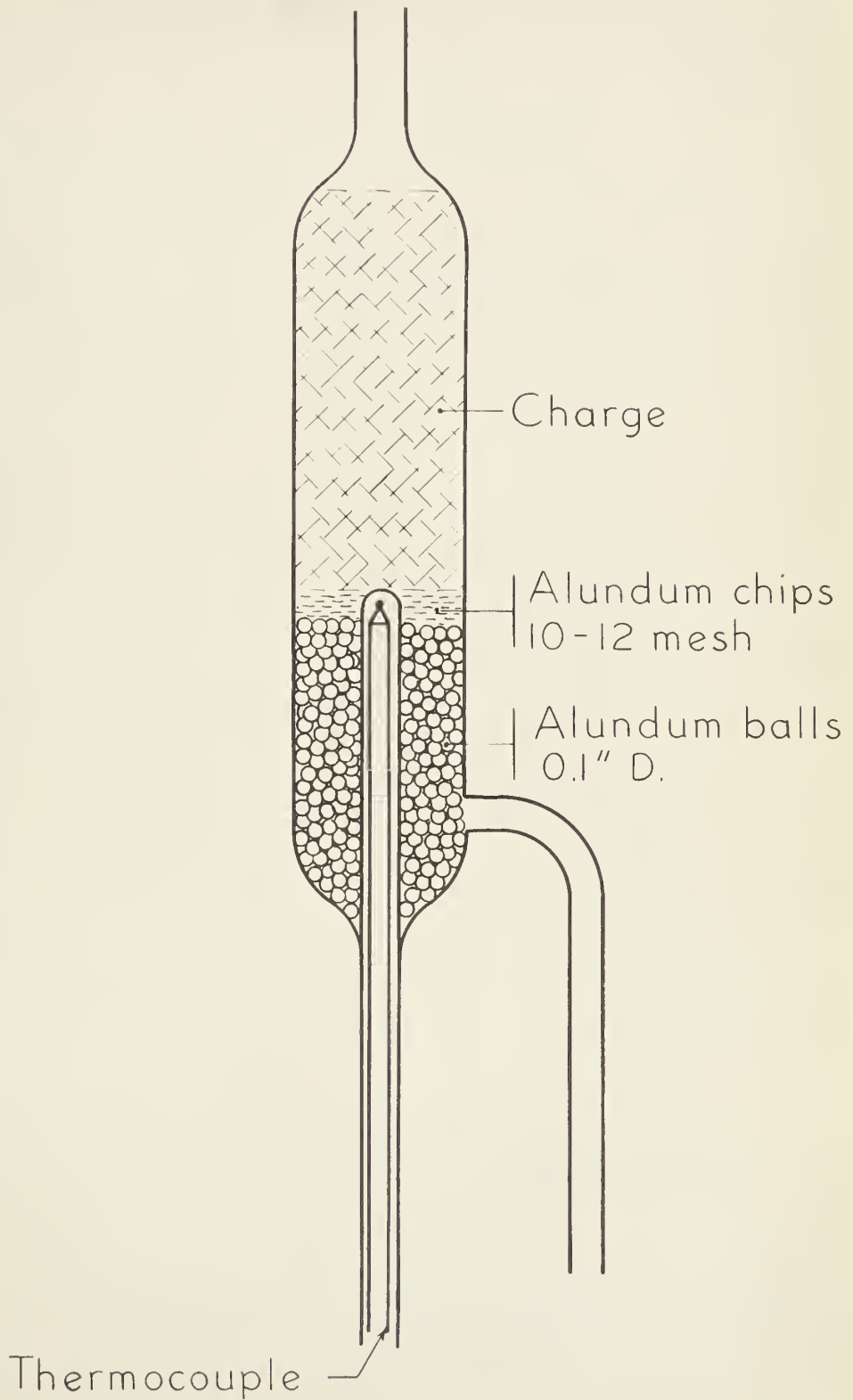


FIGURE 8

CHROMATOGRAPHICAL ANALYTICAL CIRCUIT

A. Gas Flow Circuit

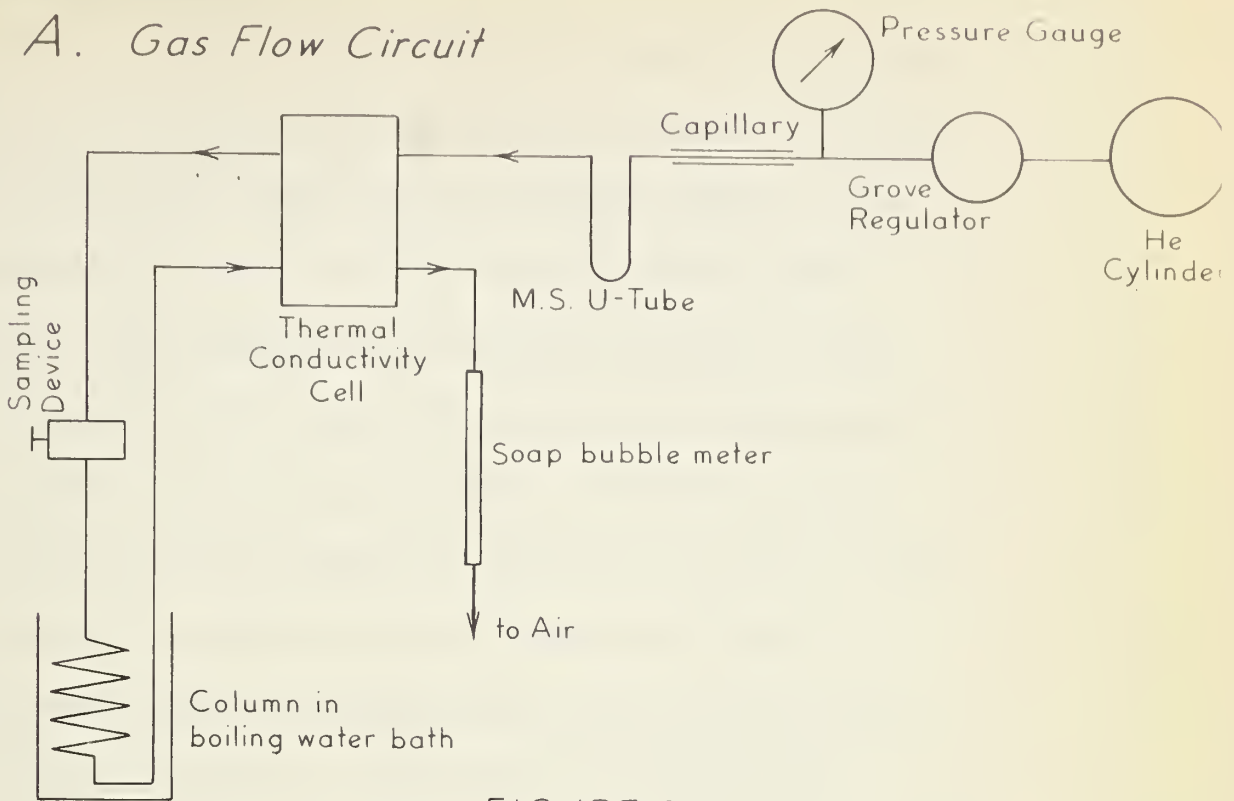


FIGURE 9

B. Electrical Circuit

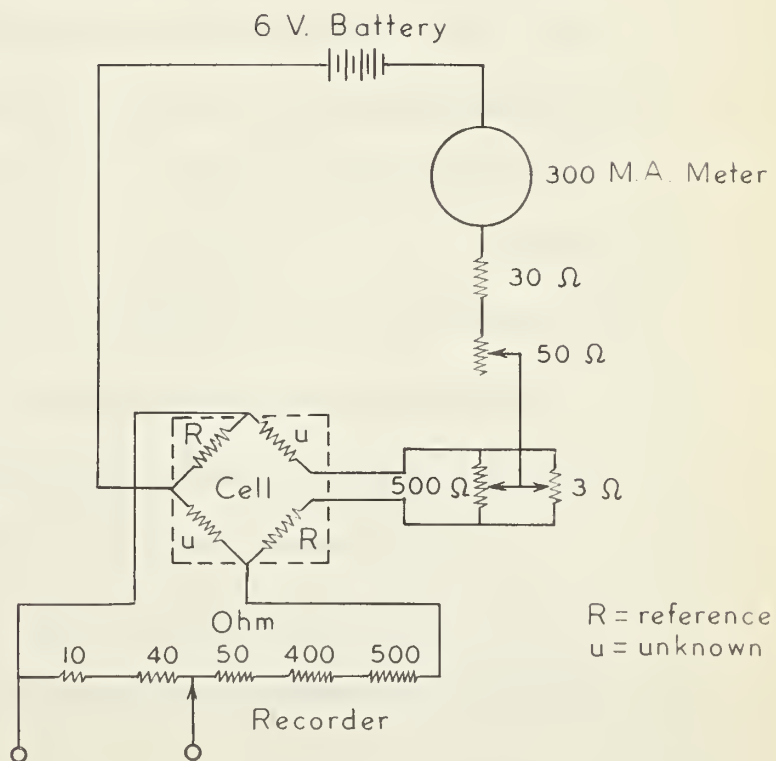


FIGURE 10

Experimental Scheme

Series A was carried out to make the conventional test for porous diffusion. Half a gram samples of charcoals Nos. 3a, 3b and 3c were mixed with six grams of ~~alundum~~ chips of the same mesh size and evacuated at 800°C for one day to clean off the surface. After calibration of the analytical apparatus, the exact concentrations of CO₂ and He in the approximately 50:50 mixture bypassing the furnace were determined. The reactor was filled with He, the CO₂ flow introduced and samples were taken for thirty minutes. The calibration was then repeated and the reactor re-evacuated at 800°C overnight after which a second run was made at a different temperature. After the third run and about 15% by weight burnoff of the carbon, a new charge was introduced.

According to Walker et al (37), heat transfer considerations showed that for a graphite rod from 800°C to 1000°C, the temperature gradients were negligible. It is possible though, that the lower thermal conductivities of the porous charcoal particles resulted in particle temperature gradients. The vertical temperature gradient was corrected for by taking the log mean temperature of the bed (the Arrhenius relationship shown in Series B justifies this). The radial temperature gradients, if any, were small due to the good thermal conductivity of the alumina at these temperatures.

Series B in which the vertical temperature gradient was greatly reduced, was carried out to compare the reactivities

of charcoals Nos. 1, 2, 3a and 4. The only other change in conditions was to reduce the pretreatment time to 3 hours.

Series C was carried out to examine the values of K_1 , K_2 and K_3 in more detail for charcoals Nos. 1, 3a and 4. In order to do this the partial pressure of carbon dioxide in the inlet gases was varied. When carbon monoxide was introduced into the inlet gases, however, the reaction was so suppressed that the range of temperature had to be considerably raised for the conversion to be measurable.

Results

The results of all the kinetic experiments together with the calculation of the rates of reaction are given in Appendix A. For Series A, the rate of reaction R gm.mol./gm.carbon/min. for the charcoals Nos. 1, 2 and 3a is plotted against time in Figs. 11, 12 and 13. The linear portions of the rate curves have been used as the characteristic reaction rates at that temperature and an Arrhenius Plot drawn, (Fig. 14). Series B results are not depicted graphically. The characteristic reaction rate has been taken as the average rate over a 15 minute interval. Runs B1 and B2 showed that the reaction was neither diffusion controlled nor a zero order one, the calculations being given in Appendix B. The reactivities of charcoals Nos. 1, 2, 3a and 4 are compared in an Arrhenius Plot, (Fig. 15). The best straight lines for the Arrhenius Plots for Series A and B were

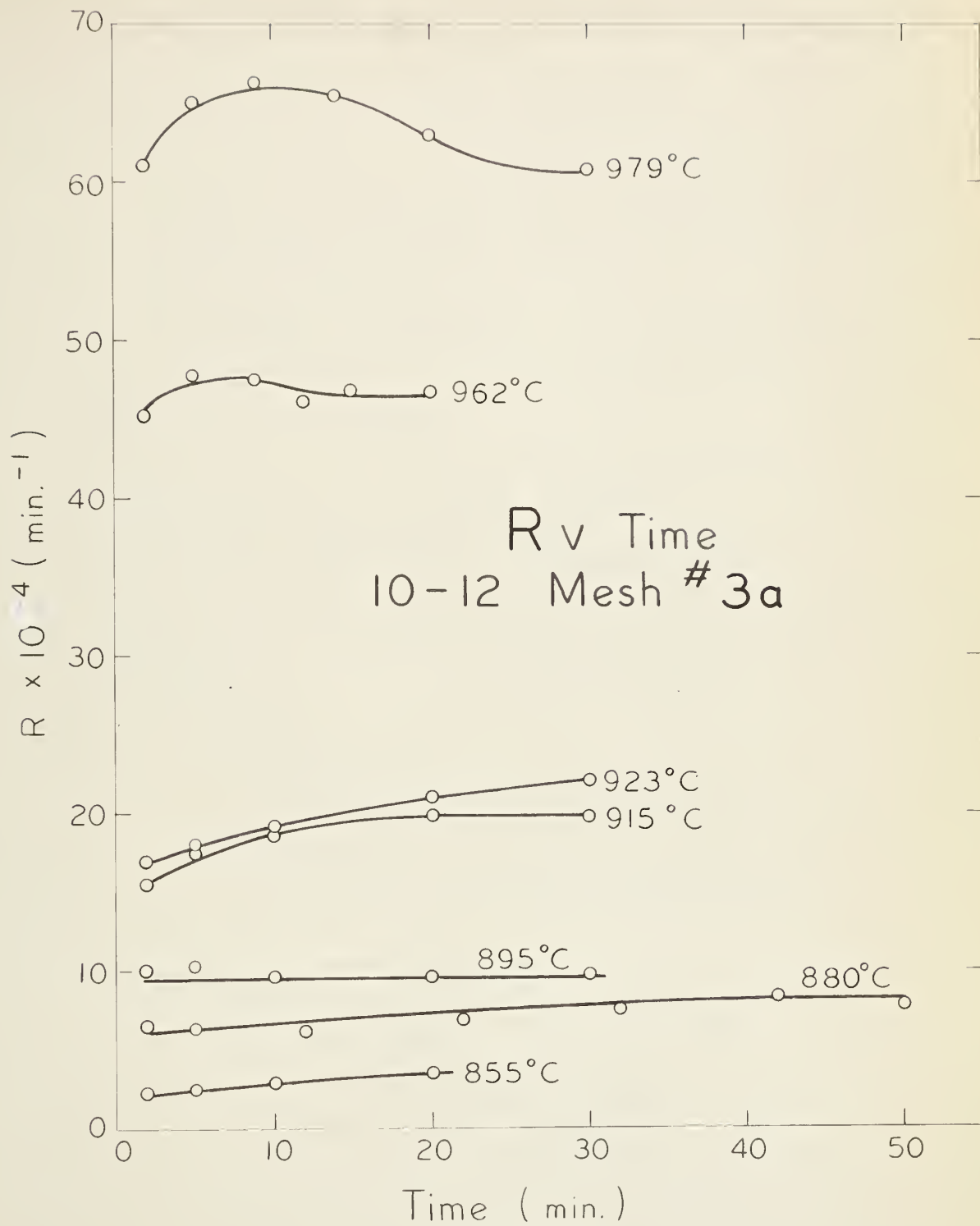


FIGURE II

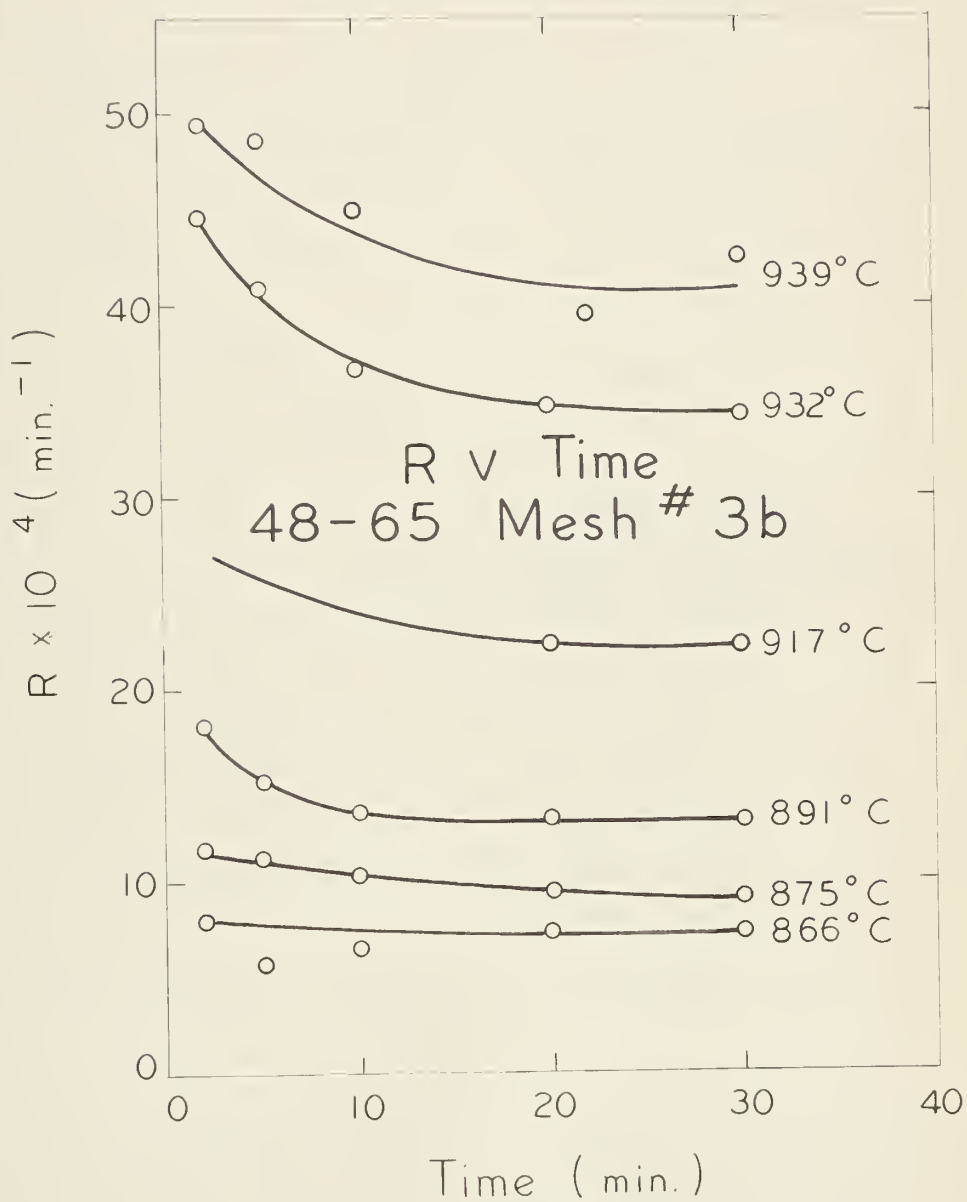


FIGURE 12

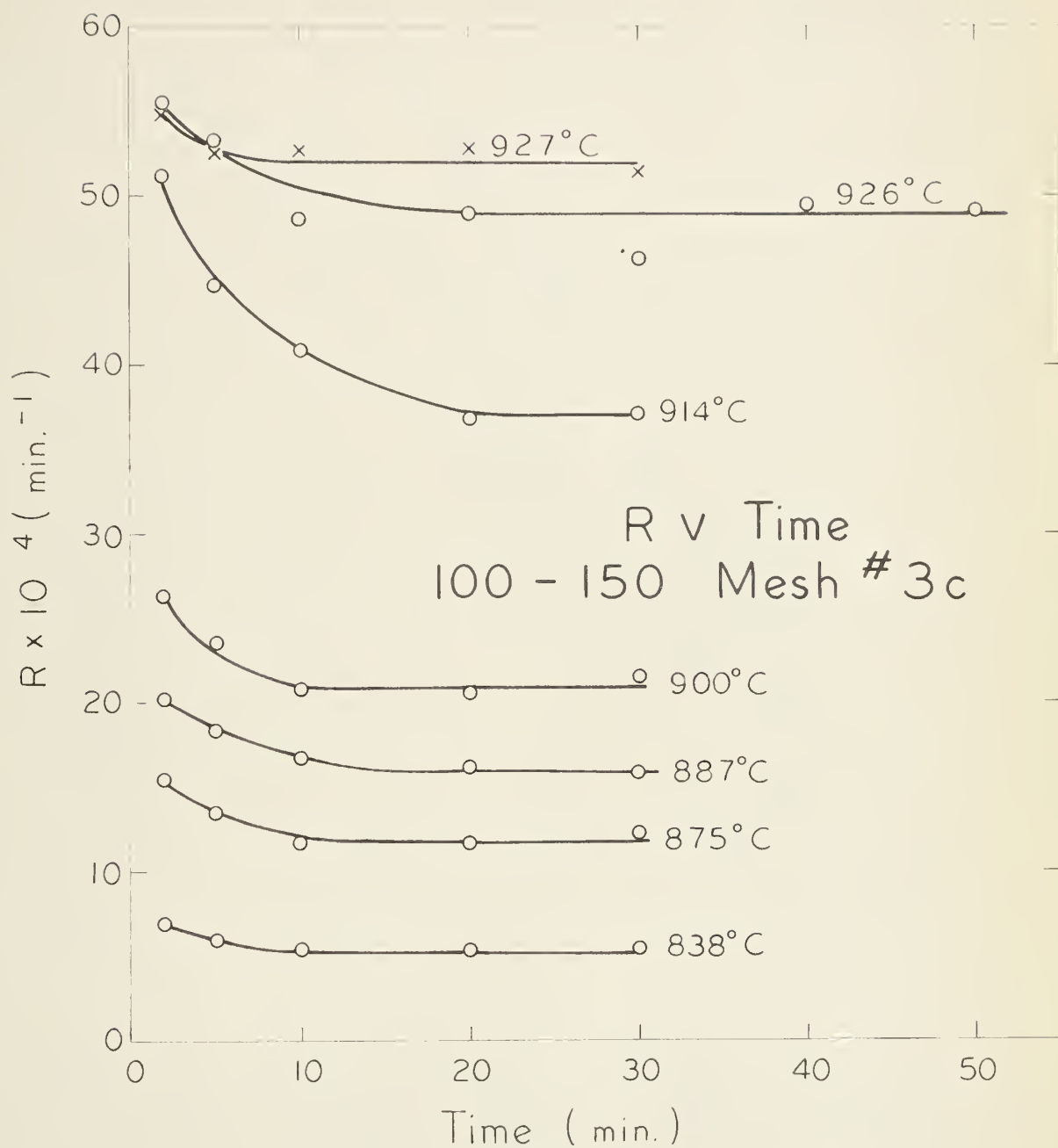


FIGURE 13

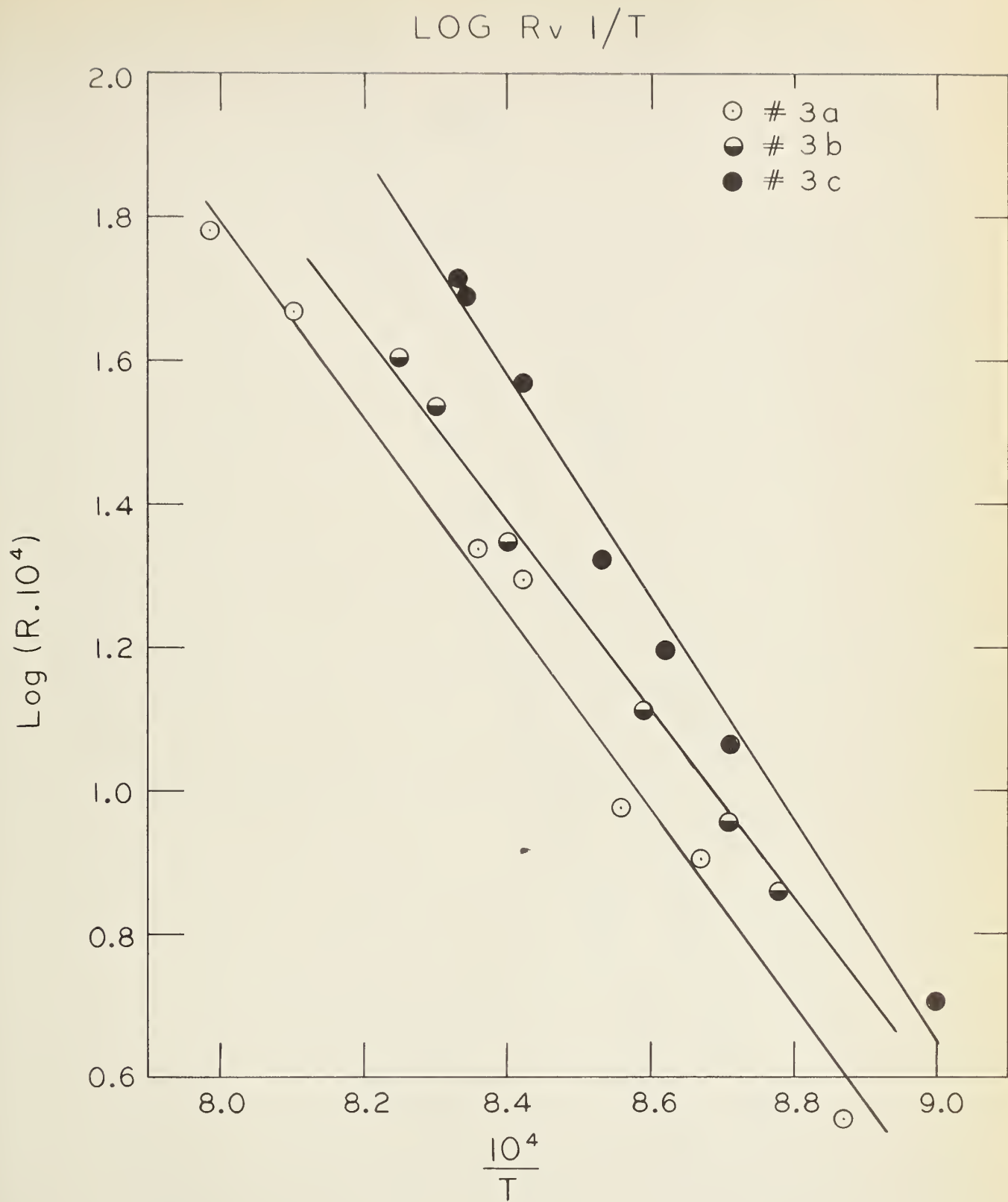
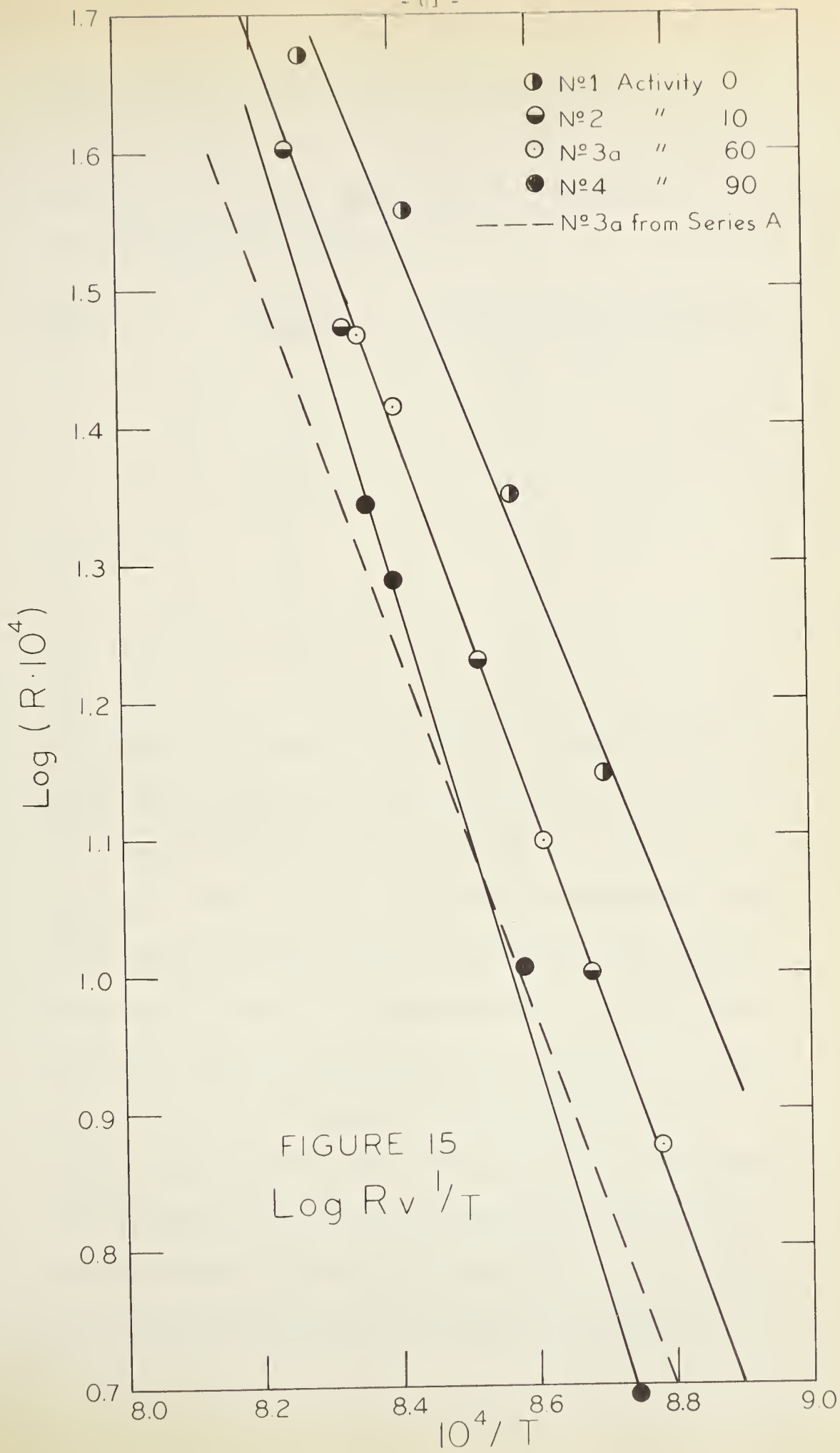


FIGURE 14



obtained using the method of least mean squares, (Appendix A.).

The method was chosen as an arbitrary one, although not statistically warranted due to the small number of points. The following

Activation Energies were obtained:

Table 11		
<u>Series</u>	<u>Sample No.</u>	<u>Activation Energy</u> kcal/gm.mole
A	3a	63
A	3b	61
A	3c	71
B	1	59
B	2	65
B	3a	65
B	4	80

The variation in gasification rate with inlet carbon dioxide pressure for the Series C experiments is shown graphically in Figs. 16 - 22.

Due to the exponential nature of K_1 , K_2 and K_3 , the system of simultaneous equations obtained by substituting the experimental data into equation (5) could not be solved. Consequently a graphical iterative procedure was used. An approximate value for K_1 was obtained using equation (6) and the data at the two lower temperatures. Values of K_1 were found by extrapolation to the upper two temperatures, using the exponential relationship. These values and the experimental data substituted into equation (5) were plotted so as to yield the best values of K_2 and K_3 . Equation (5) was then replotted using the values of K_2 at the lower two temperatures, obtained by an exponential

VARIATION OF GASIFICATION RATE WITH INLET CARBON DIOXIDE PARTIAL PRESSURE

Date: 9th -10th April 1962

Charcoal No. 1

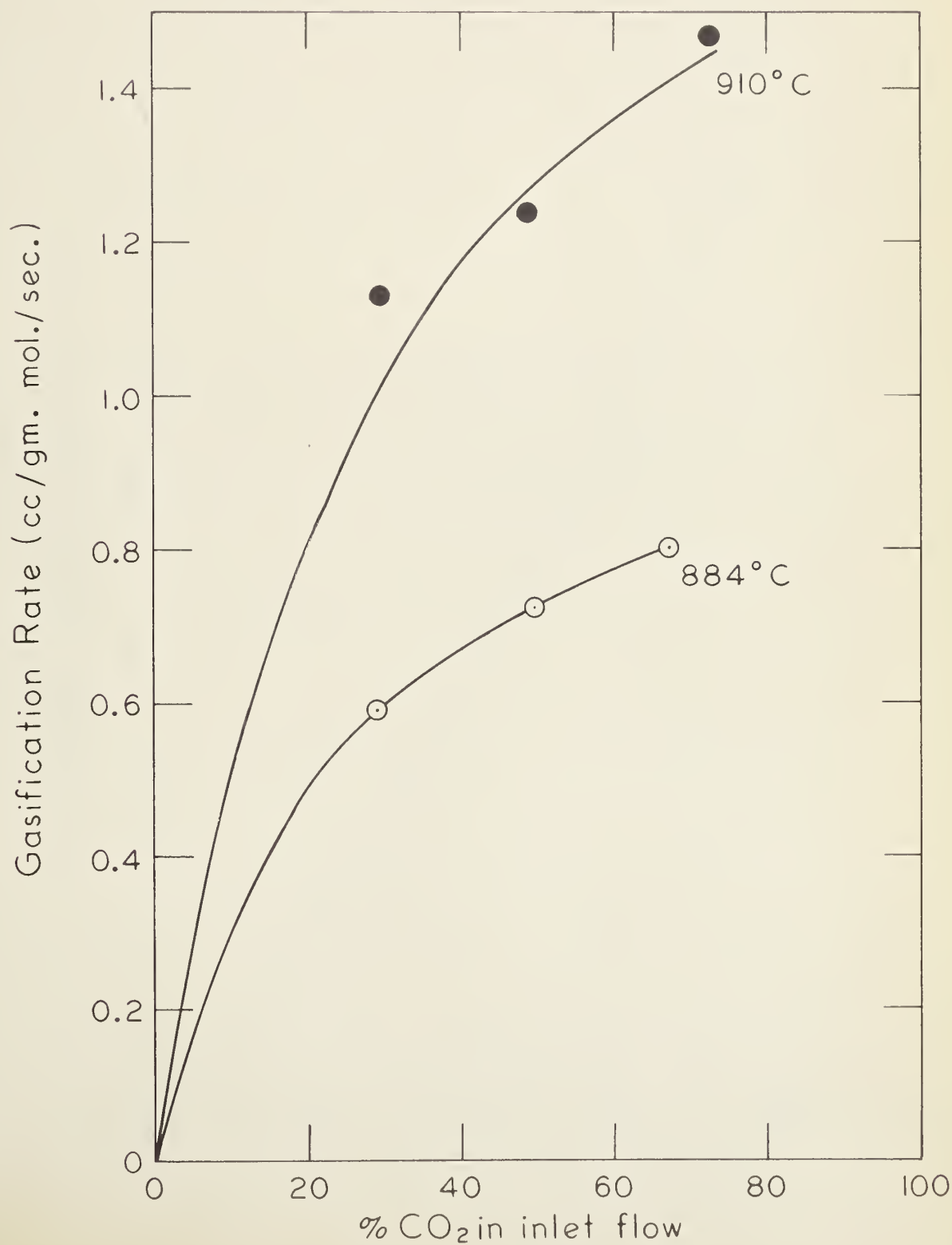


FIGURE 16

VARIATION OF GASIFICATION RATE WITH INLET
CARBON DIOXIDE PARTIAL PRESSURE

Date: 5th June 1962

938°C.

Charcoal NO.1

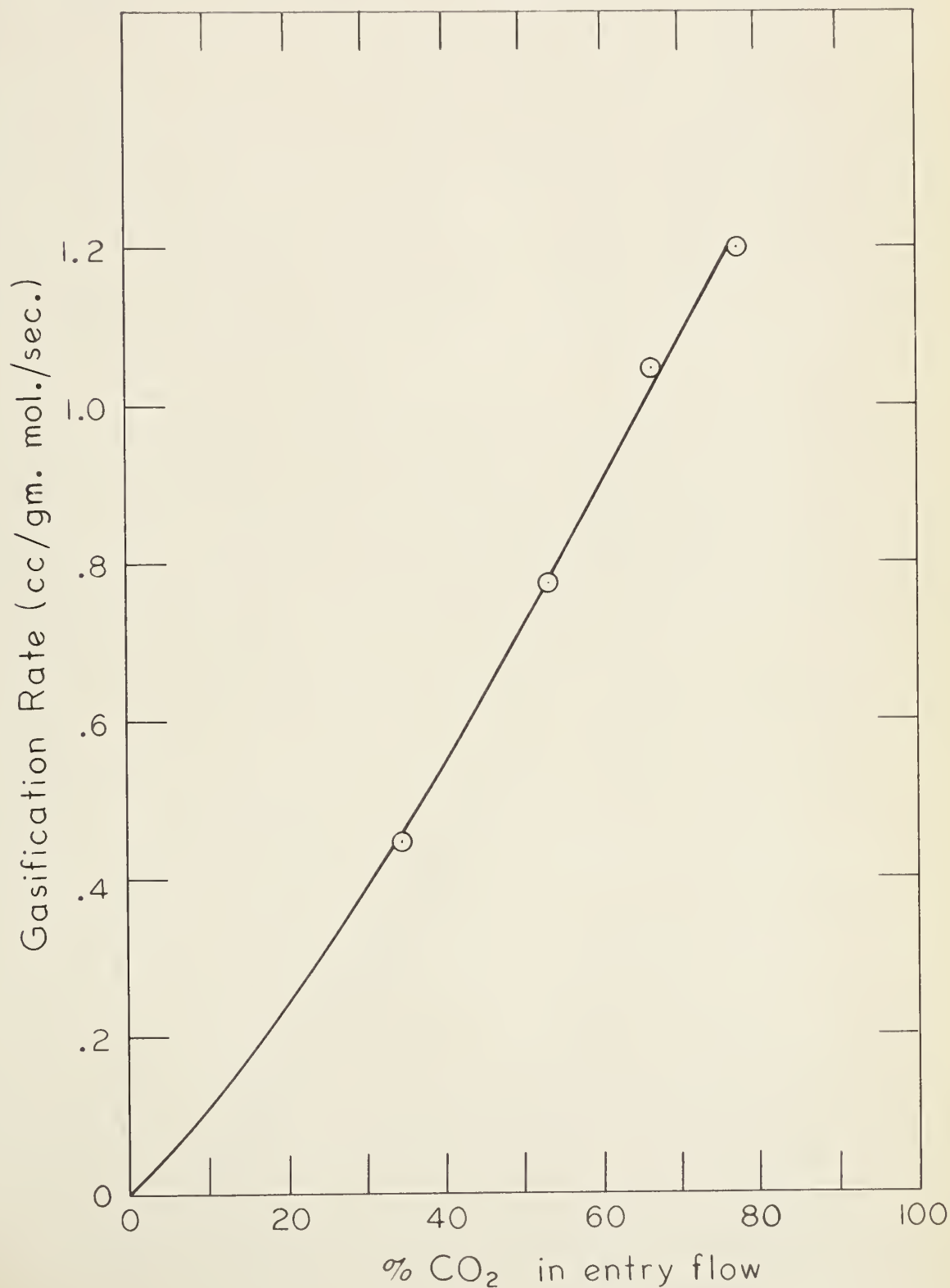


FIGURE 17

- 55 -

VARIATION OF GASIFICATION RATE WITH INLET CARBON DIOXIDE PARTIAL PRESSURE

Date: 6th June 1962

1012°C.

Charcoal NO.1

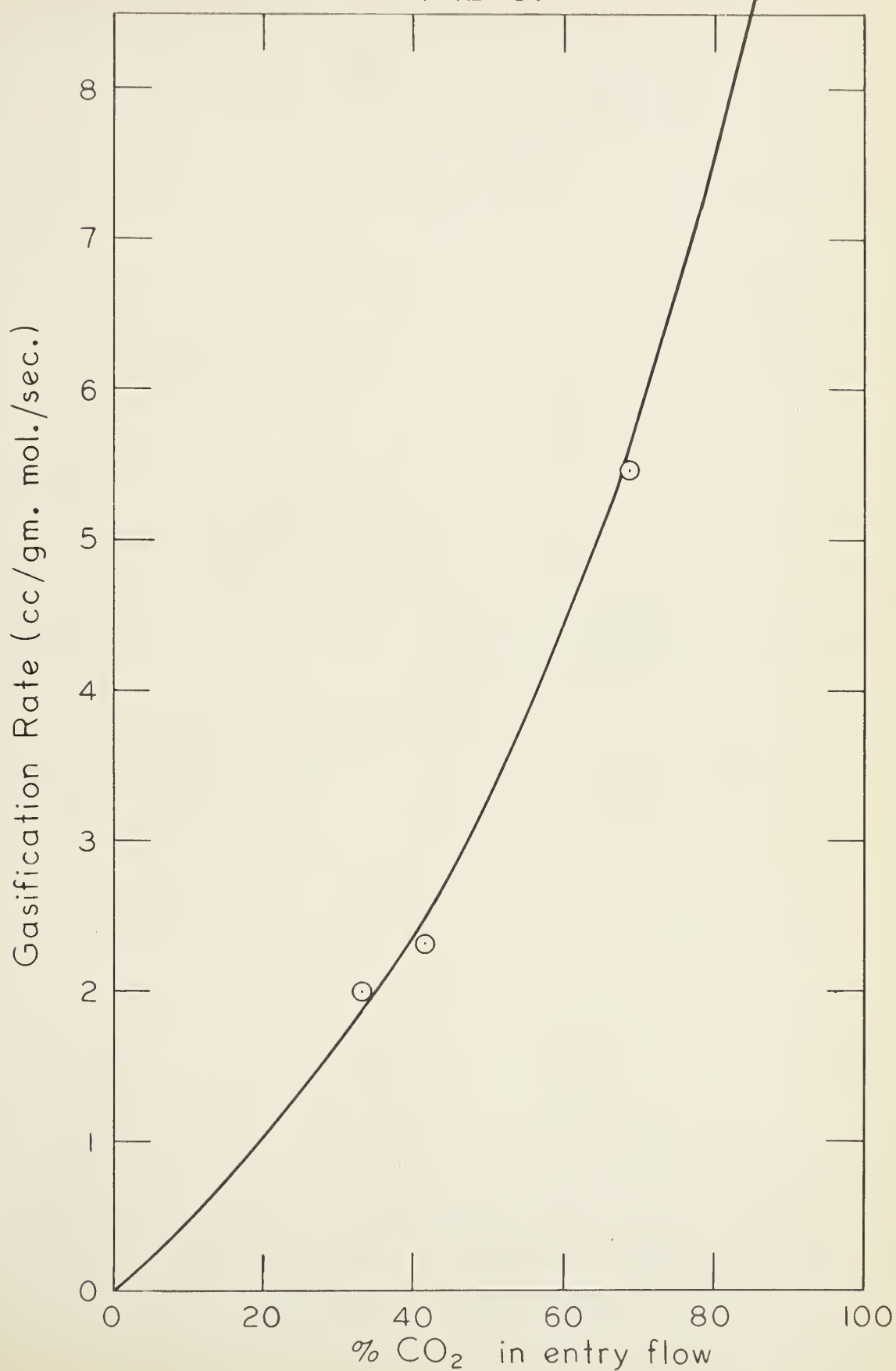


FIGURE 18

VARIATION OF GASIFICATION RATE WITH INLET CARBON DIOXIDE PARTIAL PRESSURE

Date: 4th - 8th April 1962

Charcoal NO.3a

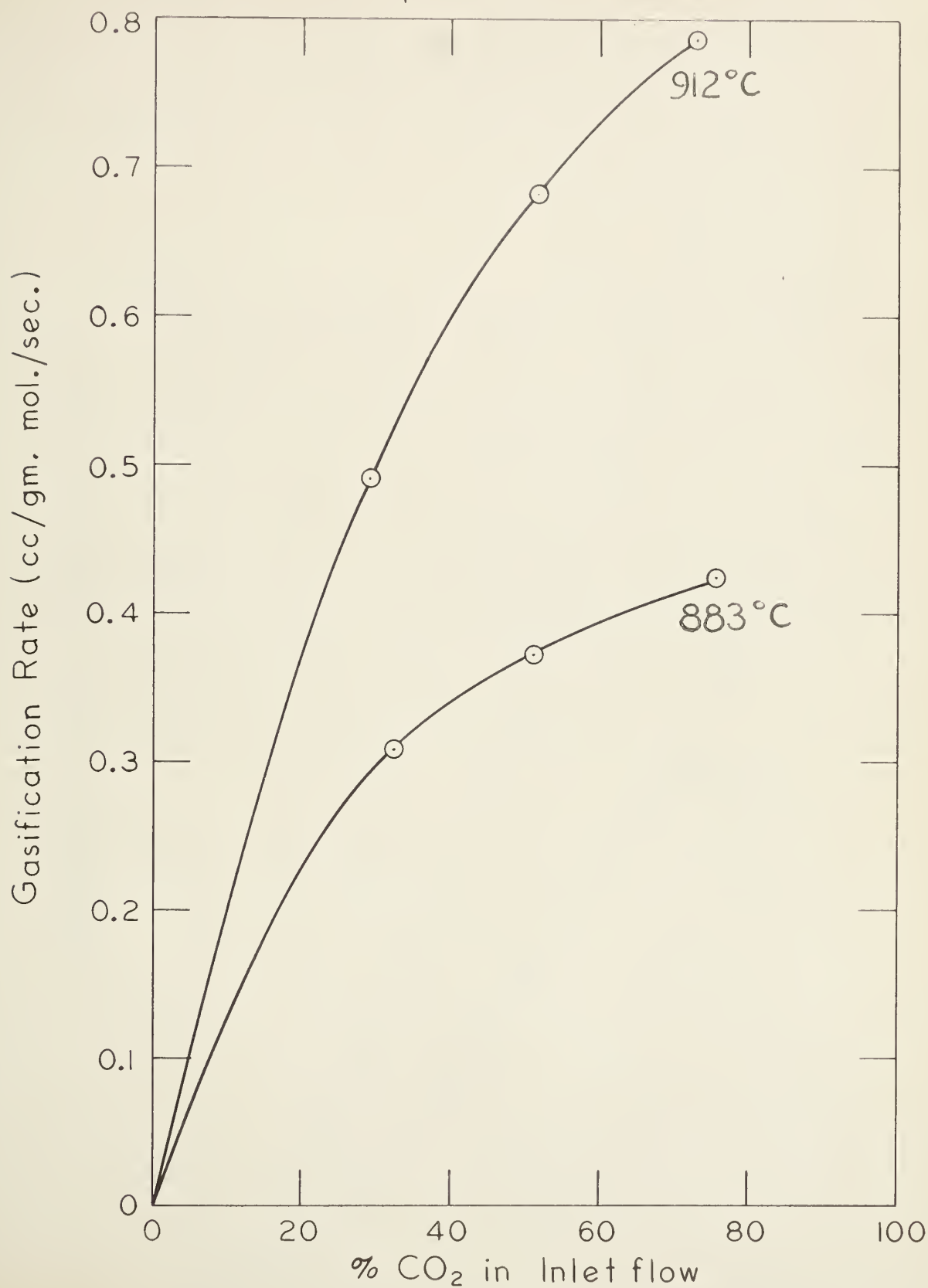


FIGURE 19

VARIATION OF GASIFICATION RATE WITH INLET CARBON DIOXIDE PARTIAL PRESSURE

-67-

Date: 11th - 16th MAY 1962

Charcoal NO.3a

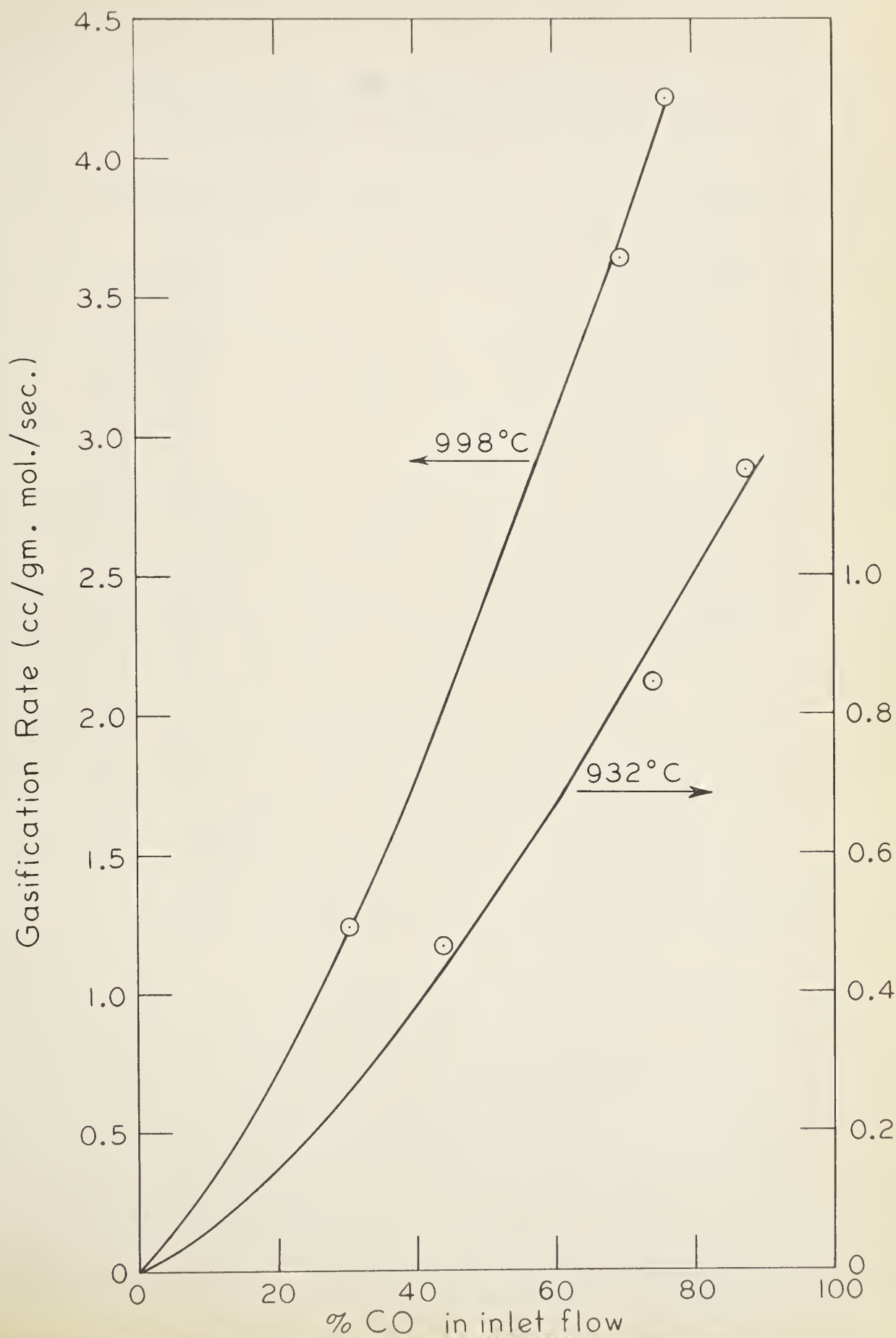


FIGURE 20

VARIATION OF GASIFICATION RATE WITH INLET CARBON DIOXIDE PARTIAL PRESSURE

Date: 12th - 13th April 1962

Charcoal NO.4

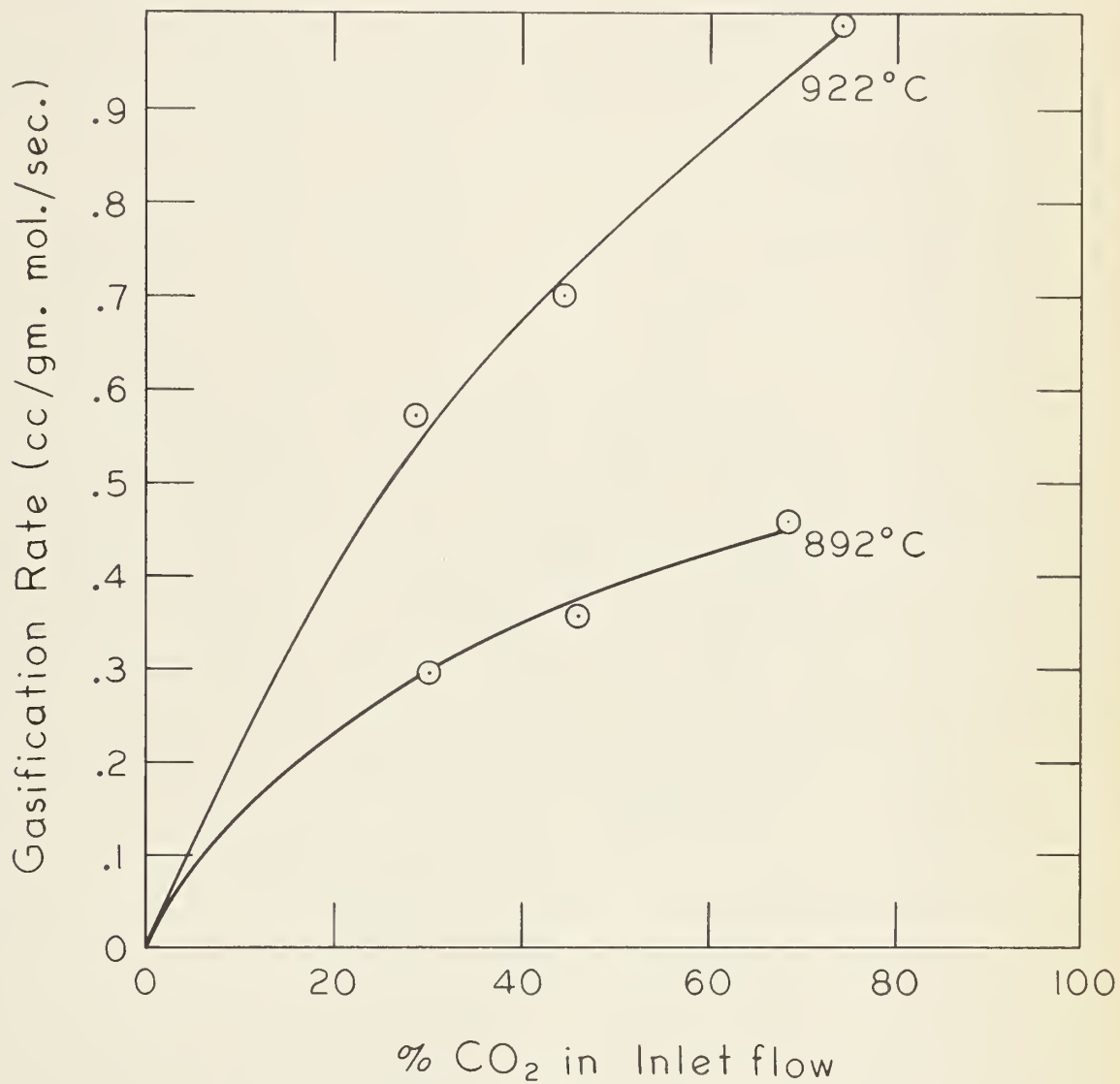


FIGURE 21

VARIATION OF GASIFICATION RATE WITH INLET CARBON DIOXIDE PARTIAL PRESSURE

Date: 22nd - 23rd May 1962

Charcoal No. 4

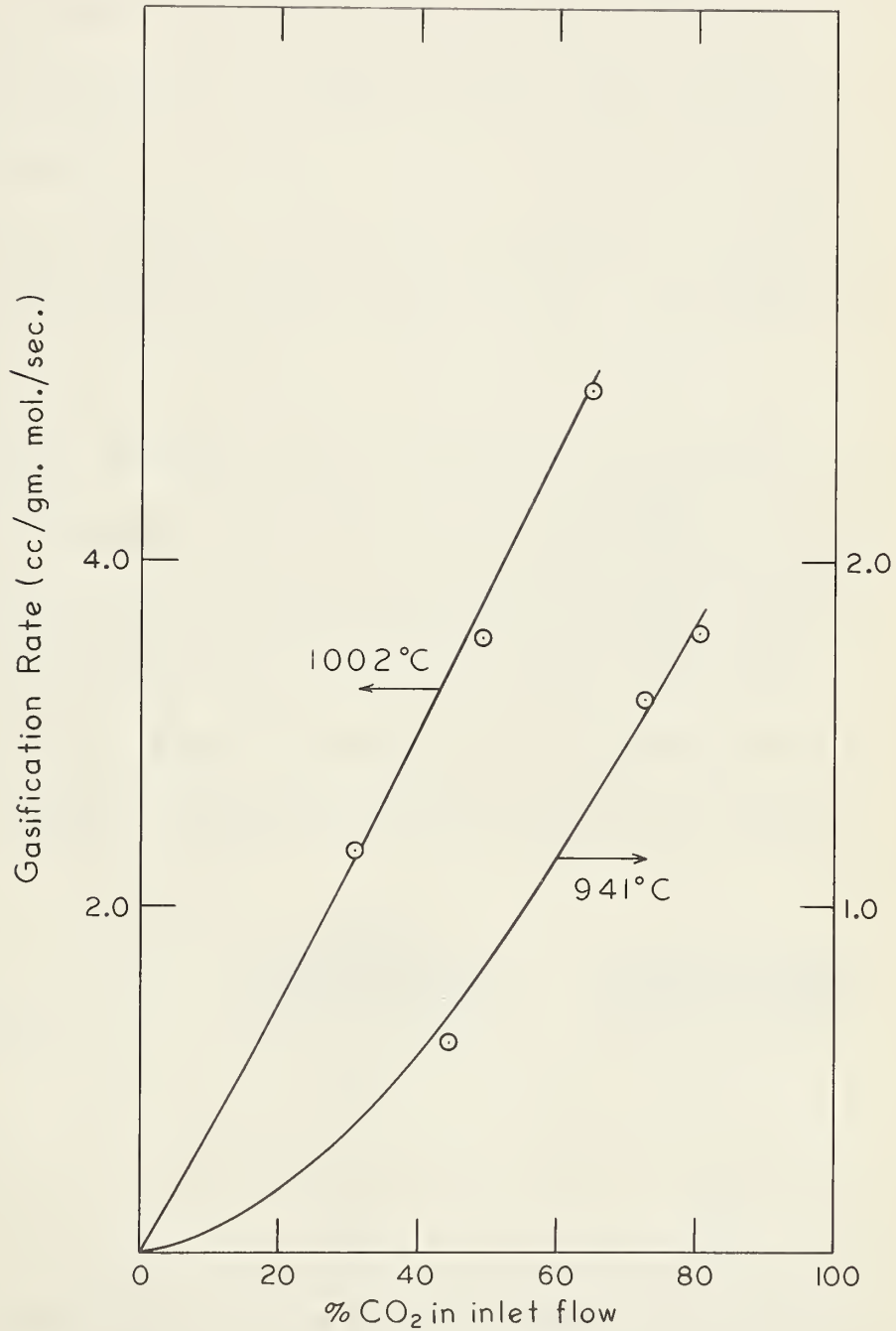


FIGURE 22

extrapolation, and the corresponding experimental data. The best values of K_1 were then used to obtain new K_2 and K_3 values and the procedure repeated. The method rapidly gave a stable solution, the details of which are given in Appendix C. It should be noted that the K_2 term is small at the lower two temperatures because no carbon monoxide gas was introduced and the K_3 term small and not too temperature dependent, see Fig. 25. Consequently the K_1 term is the most important at the lower two temperatures with the K_2 term only becoming important at the upper two. The resulting K_1 , K_2 and K_3 values are shown in Figs. 23, 24 and 25 on an Arrhenius Plot. The values of K_3 obtained from the calculation of Appendix C did not give straight lines on an Arrhenius Plot due to the smallness of the terms involved and the mode of solution which threw all the experimental errors into the K_3 term. The average value for the whole series -30 kcal/mole was consequently taken as an approximation. The Activation Energies obtained for K_1 and K_2 are:

<u>Table 12</u>		
<u>Charcoal No.</u>	<u>Activation Energy for K_1 kcal/mole</u>	<u>Activation Energy for K_2 kcal/mole</u>
1	56	- 6
3a	42	-48
4	51	-93

Series B indicates that the values for No. 2 charcoal are the same as those for No. 3a.

COMPARISON OF K_1 VALUES

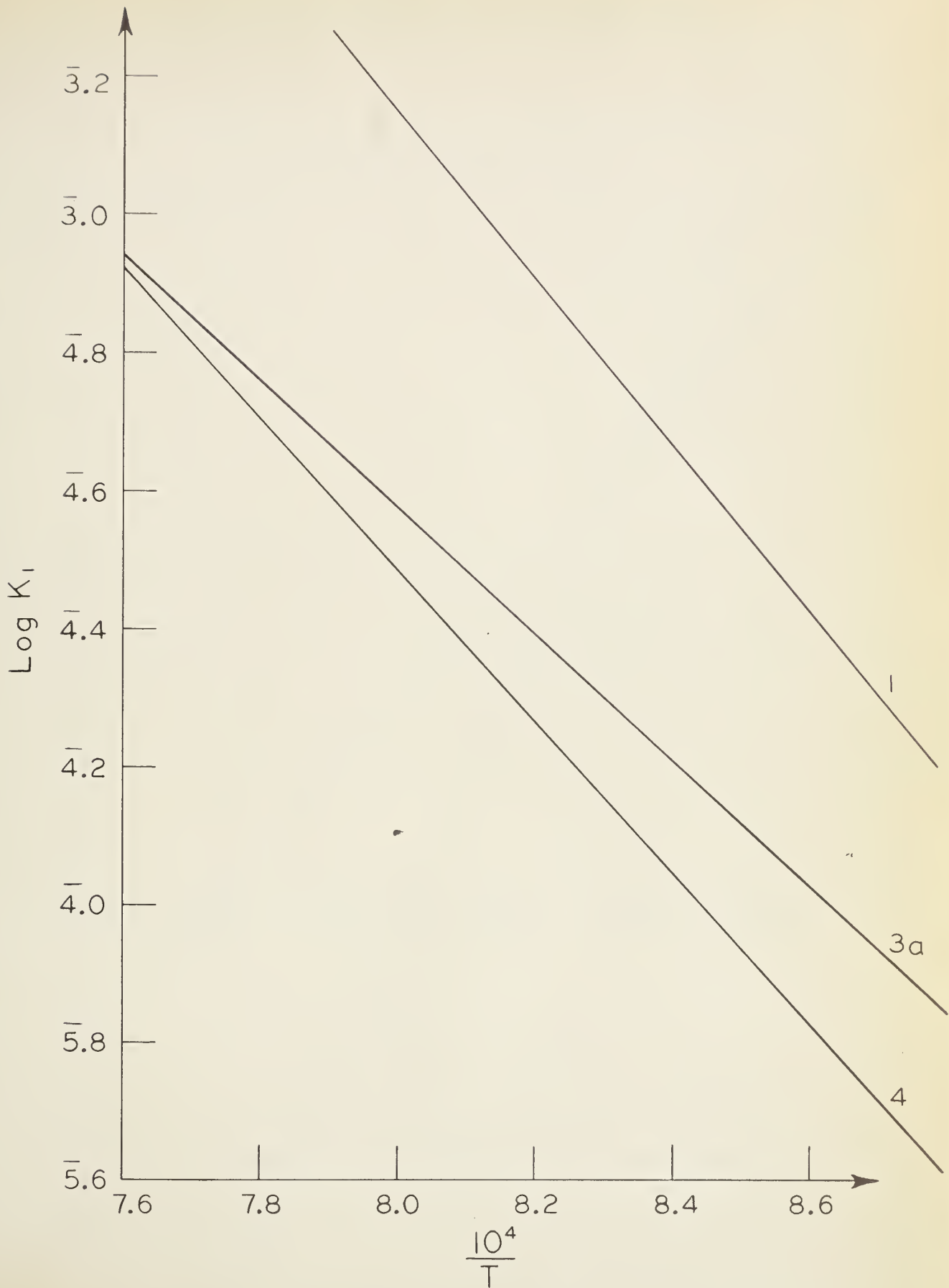


FIGURE 23

COMPARISON OF K_2 VALUES

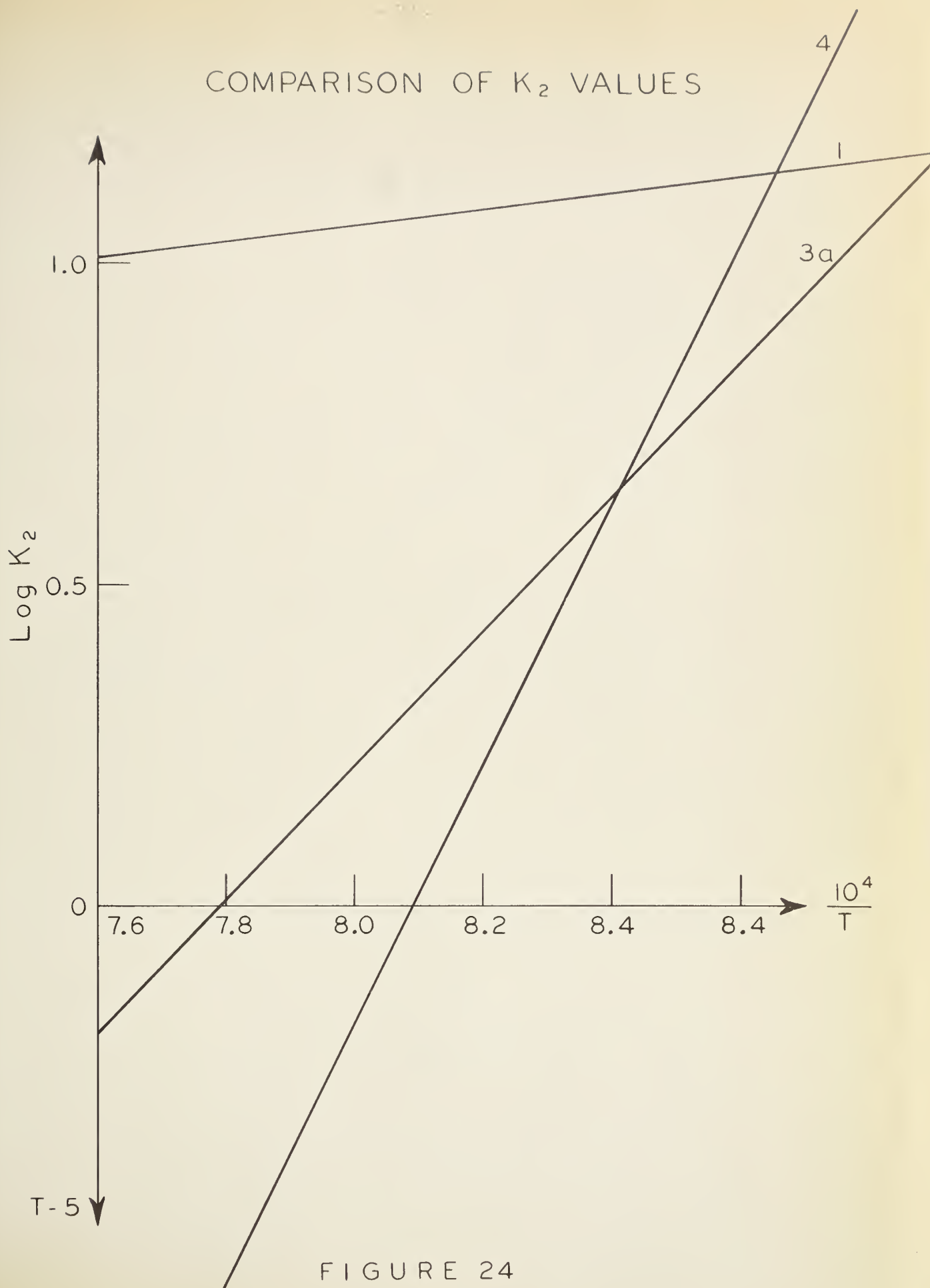


FIGURE 24

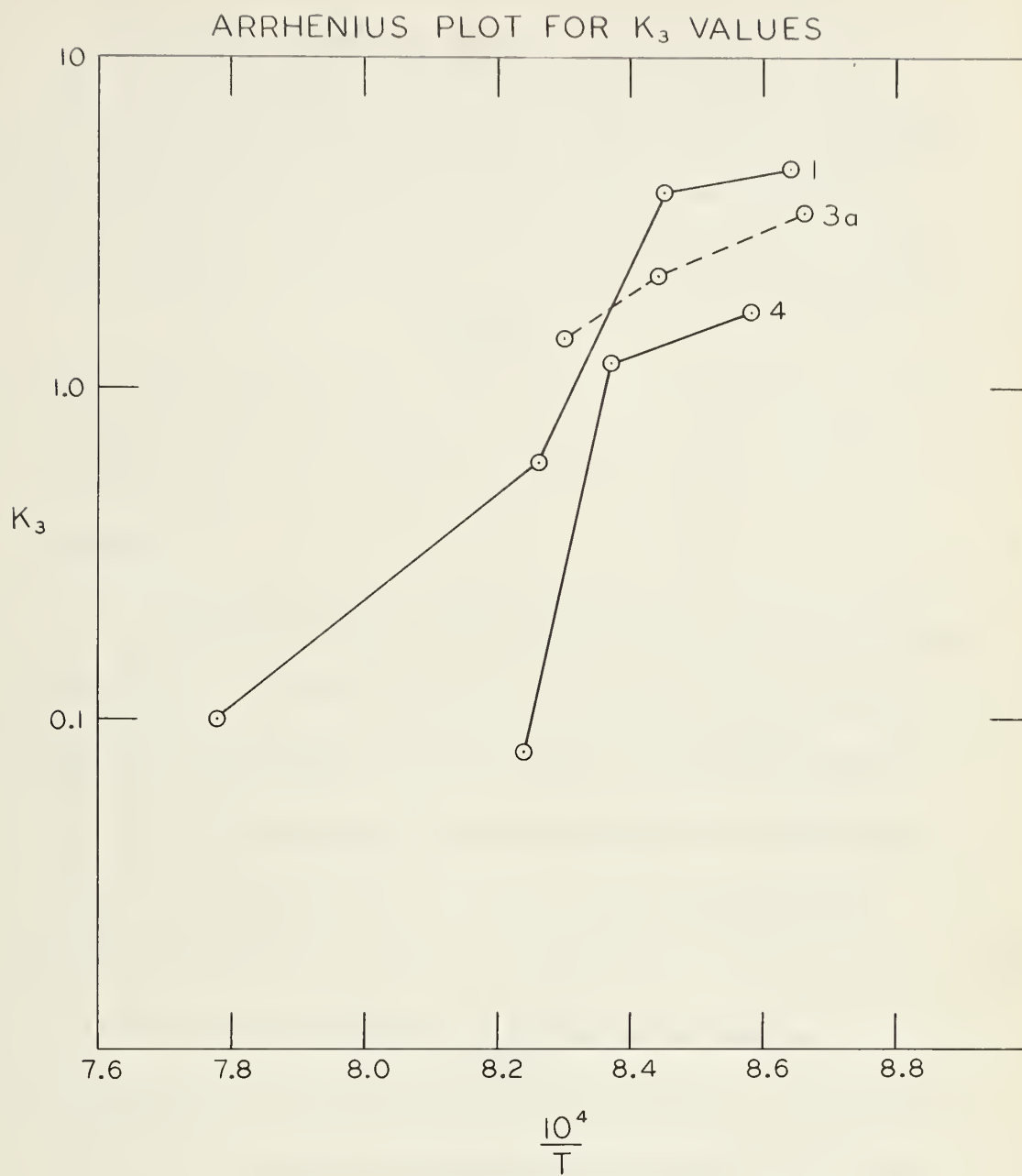


FIGURE 25

As the Activation Energies for the K_1 terms are approximately equal, the reactivity was taken arbitrarily as the value of K_1 at $10^4/T = 8.5$, i.e. 905°C (this is right in the middle of the experimental range where the K_1 term is the most significant), relative to that of No. 4 charcoal (the least reactive). Values for Nos. 3b and 3c were obtained by using values of R relative to the No. 3a value from Series A. Hence:-

Table 13

Charcoal No.	1	2	3a	3b	3c	4
Reactivity	4.1	1.5	1.5	2.1	3.1	1

Discussion

Walker et al (41) and (39) found diffusion was not controlling below 1000°C. The calculation given in Appendix B shows that the diffusion in this charcoal is mainly Knudsen, the Thiele modulus is one half and the effectiveness factor is about unity and consequently diffusion is not the slow step. In fact, if the difference in rate between Samples 3a and 3c were due to diffusion, a Thiele effectiveness factor of one half would be obtained for 3a and hence an unacceptably high activation energy of 126 kcal/mole. Consequently it has been deduced that the different reactivities of Nos. 3a, 3b and 3c shown by the Series A are due to their different natures.

The reaction rate was not proportional to the surface area of the particles because Nos. 3b and 3c with smaller surface areas per gram than No. 3a had a greater reactivity per gram. When the reaction rates were plotted as a rate per unit external area, the order of reactivity was reversed but it was not possible to assign the differences in reactivity to differences in external and macropore surface area.

Due to the opening of blind pores, large areas of No. 3a charcoal, not previously accessible, were made available for reaction during the initial burnoff (See also Sorption Experiments). Also any initial diffusion resistance would be reduced by the boring out of the pores. The concomitant poisoning of the surface by carbon monoxide resulted in the hump seen in Fig. 11. The effect was more pronounced at higher temperatures, manifesting itself as a steady increase in reaction rate at low temperatures and a more rapid one to the steady state at intermediate ones. The smaller particles of Nos. 3b and 3c charcoals apparently have a negligible number of blind pores or else the ultimate area for reaction was available before the first sample was taken.

The more highly activated charcoals have the lowest reactivity, Table 13, and extended heat treatment has the same general effect as activation, Fig. 15.

V RELATION OF REACTIVITY TO CHARCOAL PROPERTIES

Discussion

The measured properties of the charcoals are depicted graphically in Figs. 26 - 31. (Ash free) carbon, hydrogen and total acidity change markedly from No. 1 to No. 2 but much less so from No. 2 to No. 3a to No. 4 and remain roughly constant for No. 3a, No. 3b and No. 3c. Concentrations of carboxyl vary erratically. Reactivities, compared in the same figs., decrease in the series 1, 2, 4, are about the same for 2 and 3a, but again decrease in the subseries 3c, 3b and 3a. No obvious correlations exist.

Fig. (31) compares the nitrogen monolayer values, activity and heat of adsorption with the reactivity and here also no direct correlation can be seen. However, the increasing nitrogen monolayer capacities and a decreasing reactivity indicate that sorption takes place on areas not available for reaction as well the reaction sites. Steam activation clearly increases the sorption areas at the expense of the reaction sites.

There is an apparent correlation between the microscopic roughness and the reactivity as can be seen from the photographs on pages 33 and 34. The microscopic roughness extends to the submicroscopic scale because the heats of adsorption follow the same trend. Habgood & Hanlan (17) attributed the higher heats of adsorption to attraction by two surfaces and this is only possible if the surface is more irregular. The increase in chloropicrin

COMPARISON OF CHARCOAL PROPERTIES

FIGURE 26

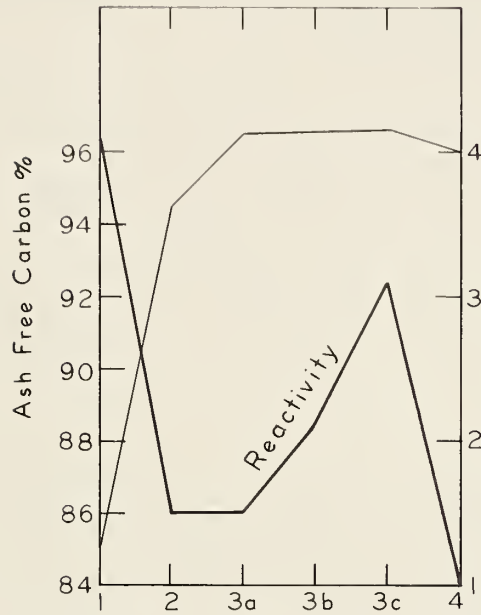


FIGURE 27



FIGURE 28

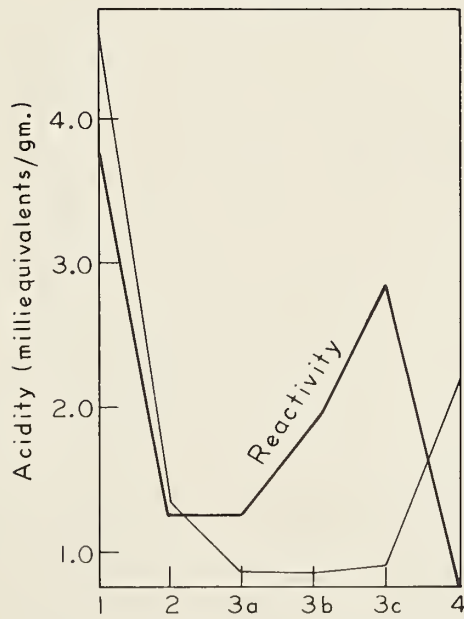
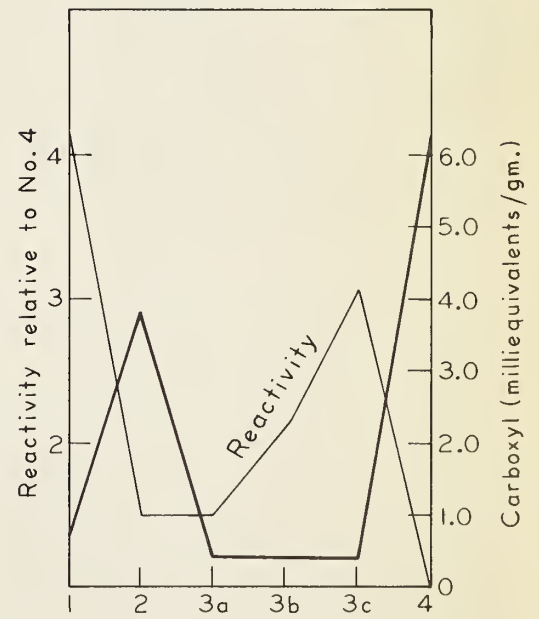


FIGURE 29



COMPARISON OF CHARCOAL PROPERTIES

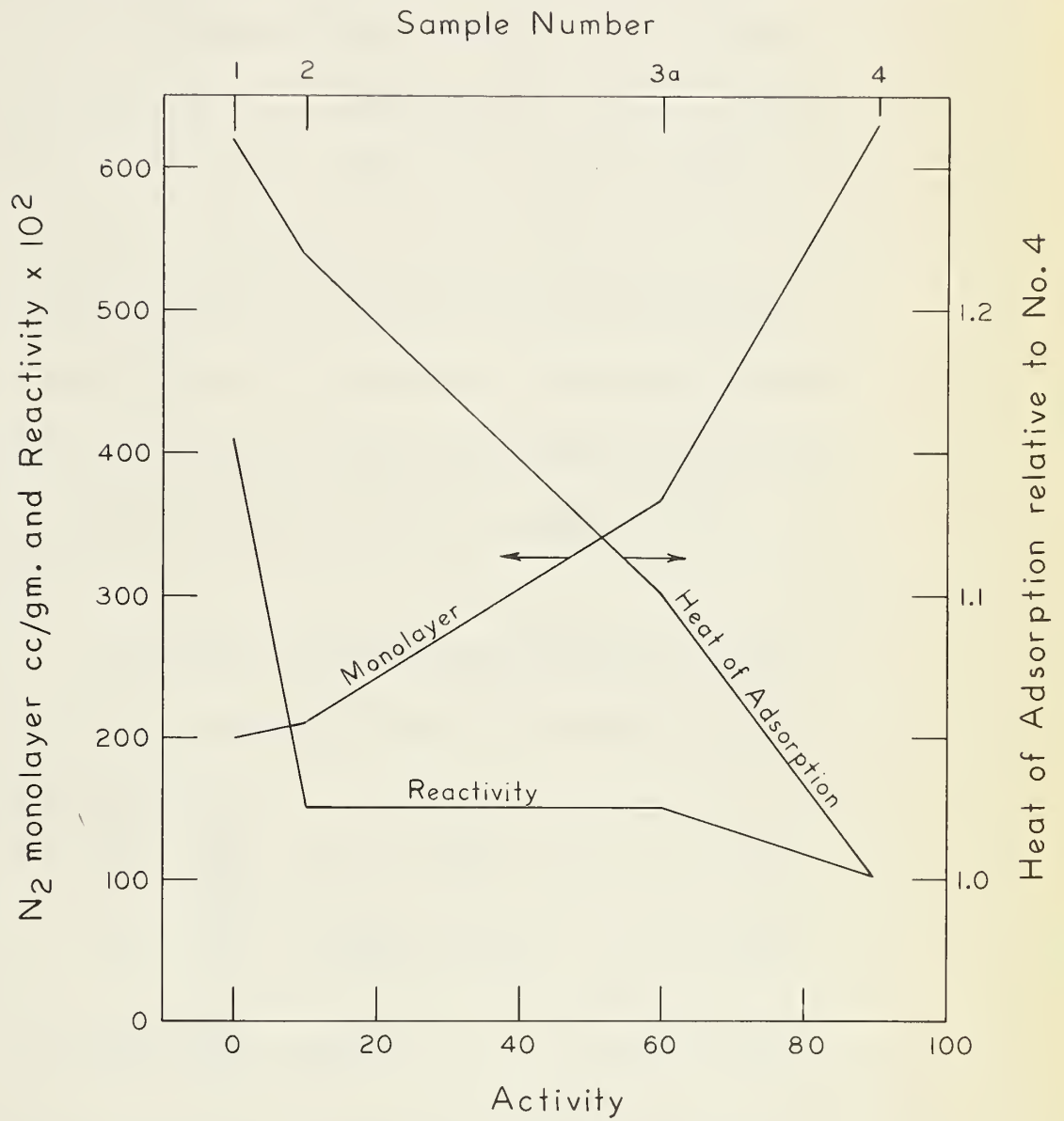
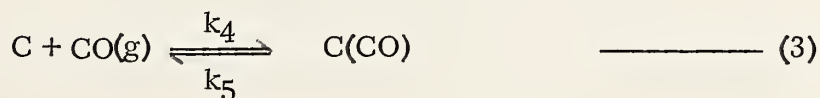
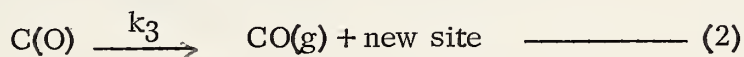
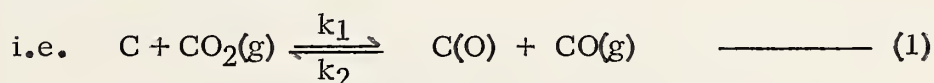


FIGURE 31

activity may be similarly explained, the large molecule being barred from much of the surface by its irregularities in the case of the less highly activated charcoals. With increasing steam activation, the crevices and bottlenecks in the pore spaces are eaten out, thus making more surface accessible. Of course, the line of demarcation between a highly irregular surface and a fine pore system cannot be clear. This roughness will also explain why the least activated charcoal is the most reactive. The literature survey (pages 23 and 24) showed that the edge carbon atoms of the lamellae are the most reactive, the irregular surfaces will expose more edges and will thus have a greater reactivity than the bored out and smoothed surfaces of more highly activated charcoals.

The scheme of equations representing the reduction is the same as that of Mechanism III due to Semechkova & Frank Kamenetzky, see page 13.



Equation (3) only refers to an equilibrium on the same sites as reaction (1) i.e. blocking of the sites by carbon monoxide. In general an adsorption equilibrium will exist on more than the chemically reactive sites which could be represented by an

equation such as (3). For a flow system, after the adsorption equilibrium is reached on these other sites, it will not affect the equilibrium and may be neglected in the derivation of the flow equation.

Let the total concentration of reactive sites be L ,

the fraction covered by (O) be a

and by (CO) be b .

At the steady reaction rate the concentration of each of these surface species will be constant and their balance is given by

$$k_1 L(1 - a - b) P_{CO_2} - k_2 L a P_{CO} - k_3 L a = 0 \text{ for } (O) \quad (4)$$

$$k_4 L(1 - a - b) P_{CO} - k_5 L b = 0 \text{ for } (CO) \quad (5)$$

Eliminating b from (4) and (5) gives

$$a = \frac{k_1 k_5 P_{CO_2}}{k_3 k_5 + k_1 k_5 P_{CO_2} + (k_2 k_5 + k_3 k_4) P_{CO} + k_2 k_4 P_{CO}^2} \quad (6)$$

$$\text{The rate of reaction } R = k_3 L a \quad (7)$$

(6) and (7) give

$$R = \frac{k_1 L P_{CO_2}}{1 + \frac{k_1}{k_3} P_{CO_2} + \left\{ \frac{k_2}{k_3} + \frac{k_4}{k_5} \right\} P_{CO} + \frac{k_2}{k_3} \frac{k_4}{k_5} P_{CO}^2} \quad (8)$$

If either of the two retarding mechanisms, i.e., blocking of sites or the reverse of reaction (1), does not occur, the final rate equation becomes that of Mechanism I or II. Even for intermediate cases, equation (8) will have the same form as the general rate equation for small values of the last term in the denominator. Consequently, as it seems most likely that carbon

monoxide is adsorbed onto the reactive sites but nevertheless Mechanism II is operative for some charcoals, this mechanism appears to be the more general case. The general rate equation was found to satisfactorily correlate the experimental results although K_3 could not be obtained with any degree of accuracy because the term containing it was small and the mode of calculation threw all the errors into the K_3 term, including that of assuming an Arrhenius relationship for K_2 . The activation energies in kcal/gm. mole for the various velocity constants for Mechanisms I and II are tabulated below:

TABLE 14

Mechanism:	I			II		
Charcoal No.	k_1L	k_4/k_5	k_1/k_3	k_1L	k_2L	k_3L
1	56	- 6	-30	56	80	86
3a	42	-48	-30	42	24	72
4	51	-93	-30	51	-12	81

It can be seen that the temperature coefficient for k_1L is the same for both mechanisms and within the limits of experimental error, the same for all the charcoals. This could reflect a different concentration of sites in each charcoal, a different concentration of the more reactive sites with the changing concentration of less reactive sites being masked or a complex interaction between k_1 and L . As other investigators (41) have found different activation energies, the latter explanation is preferred. The wide variation in the temperature

coefficient of k_2L for Mechanism II and k_4/k_5 for Mechanism I may be explained as due to the relative importance of the two methods of carbon monoxide retardation. For charcoal #1, retardation will be by reaction (1) reverse and hence Mechanism II will be applicable (derived by Reif (28) for a high temperature coke). For charcoal #4, retardation will be by blocking of sites and Mechanism I will be applicable. This mechanism was derived by Gadsby et al (15) for a highly activated coconut char. One of their objections to Mechanism II was the low negative value obtained for the activation energy of k_2L which seemed improbable for the reaction represented. The table shows a low negative activation energy for k_2L by Mechanism II but a high negative value for k_4/k_5 by Mechanism I. Charcoal #3a is intermediate. Such a mechanism readily explains the existence of the two opposing mechanisms.

The high negative temperature coefficient for k_4/k_5 indicates that reaction (3) is not a ~~physical~~ adsorption but the equilibrium of a surface oxide. The concentration of sites L in charcoal is frequently left as an integral part of k_3 in equation (7), e.g., all the Mechanisms in the Introduction do this. It will be a balance between thermal annealing and the formation of new sites by reaction. The more irregular charcoal would be expected to have more of these sites as the edge atoms have the greatest reactivity and this is borne out by the experiments reported here. The relative

importance of the two retarding mechanisms is apparently related to the surface geometry of the charcoal. The charcoal with the highly irregular surface reacts relatively unhindered by monoxide blocking of sites whereas that with the smooth surface reacts relatively unhindered by reaction (1) reverse i.e., the amount of blocking depends on the neighbourhood.

The variation in heat treatment is readily explained by the same model, the heat treatment causing a smoothing out of the surface and hence a lower reactivity.

The increase in reactivity found in the smaller particles is due to a sorting process. The steam activation is not completely uniform throughout the particles and material relatively highly activated, but with lower reactivity would have larger pores than the average. This, during grinding, will more readily become dust and the particles left will consist of the denser material with a greater internal roughness and reactivity than the starting material. Grinding itself also gives a rougher charcoal surface. The photographs show that the 48-65 mesh and 100-150 mesh fractions have a more irregular surface than the 10-12.

Conclusions

Charcoals are heterogeneous materials and the reduction of carbon dioxide upon them may occur at more than one kind of site. The more reactive charcoal has a rougher

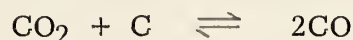
surface which is smoothed out by steam activation to yield a less reactive charcoal with a much greater internal surface area. Prolonged heat treatment also has this effect.

Mechanism III due to Semechkova and Frank Kamenetzky (31) is compatible with the experimental evidence, Mechanisms I and II ((15) and (29)) are probably particular cases. The predominant mode of retardation by carbon monoxide depends on the surface geometry, blocking of sites characterizing the smooth charcoal and recombination of carbon monoxide with surface oxide characterizing the rough charcoal in these experiments.

APPENDIX A

Calculation of Results for Series A

The analytical data for carbon monoxide and dioxide were tabulated as a ratio (G) to minimize variations in the analytical circuit.



In 1

Out 1 - x 2x

If x vol. CO_2 converted per 1 vol. CO_2 entering reactor, then $(G) = \frac{2x}{1-x}$

The ratio of CO out/ CO_2 in, is required $(H) = 2x$

$$(H) = \frac{(G)}{1 + (G)/2}$$

Rate of CO formation = $(H) \cdot f$ cc./sec.

where f = rate of flow of CO_2 in (cc./sec.)

Rate of gasification of carbon as CO = $\frac{(H) \cdot f}{2}$ cc./sec.

$$= \frac{(H) \cdot f}{2} \cdot \frac{12}{22,400} \text{ gm. C/sec.}$$

∴ Concentration of carbon (C) remaining at time t mins is given by

$$(C) = 0.5 -$$

$$\frac{12 \cdot f \cdot 1 \cdot 60}{22,400 \cdot 2} \cdot \sum_0^t (H) \cdot \Delta t \text{ gm.}$$

(this allows for a changing rate of reaction)

∴ Rate of gasification of carbon (R) gm./gm. carbon/sec. given by

$$R = \frac{(H) \cdot f}{2} \cdot \frac{12}{22,400} \cdot 0.5 - \frac{12}{22,400} \cdot \frac{f}{2} \cdot 60 \sum_0^t (H) \cdot \Delta t \text{ sec}^{-1}$$

$$R = (H) \cdot \left(\frac{31.1}{f} \right) - \sum_0^t (H) \cdot \Delta t \cdot \text{min}^{-1} \text{ (column 1)}$$

Results		A Series		#3a Charcoal				
A	B	C	D	E	F	G	H	I
Date	Mesh	Time (mins)	Flow rate (cc/sec)	Temp. (°C)	CO ₂ % in	CO out CO ₂ out	CO out CO ₂ in	R x 10 ⁴ (min ⁻¹)
Ap. 14	10-12	0	1.000		51.1			
		2	1.000	877		.0400	.0392	6.50
		5				.0382	.0375	6.23
		12				.0374	.0367	6.14
		22	1.0002	881		.0419	.0410	6.90
		32	1.006	881		.0455	.0445	7.52
		42	1.006	884		.0504	.0491	8.39
		52	1.006	884		.0471	.0460	7.91
			1.000		51.9			
Ap. 17	10-12	0	1.000		48.3			
		2		922		.1081	.1027	17.0
		5		922		.1150	.1089	18.1
		10	1.028			.1194	.1128	18.95
		20		923		.1306	.1225	21.0
		30	1.040	923		.1338	.1253	21.9
			1.002		50.6			
May 23	10-12	0	1.000		53.5			
		2		961		.309	.2675	45.3
		5				.323	.2775	47.6
		9				.314	.271	47.4
		12		962		.299	.260	46.1
		15				.300	.261	46.9
		20				.291	.254	46.8
			.990		51.5			
May 24	10-12	0	.995		53.6			
		2				.011	.011	2.1
		5		855		.012	.012	2.3
		10				.015	.015	2.8
		21	.995			.015	.015	2.9
May 25	10-12	0	1.000		52.1			
		2		979		.389	.3255	61.0
		5	1.086			.411	.341	65.1
		9				.406	.3375	66.2
		14				.385	.3225	65.5
		20	1.079	979		.353	.300	63.1
		30				.3135	.271	60.8
					52.2			
Sept. 12	10-12	0	1.000	897	54.8			
		2				.0601	.0584	10.0
		5	.978			.0614	.0596	10.2
		10	.973	895		.0572	.0556	9.6
		20				.0565	.0549	9.6
		30		893		.0564	.0548	9.7
			.951		54.2			
Sept. 13	10-12	0	.990	915	50.5			
		2				.0959	.0915	15.5
		5	1.011	915		.1084	.1029	17.5
		10	1.011			.1164	.1100	18.9
		20		915		.1195	.1127	19.7
		30	1.004			.1174	.1109	19.8
			.984		52.7			

(* At end of run, the carbon particles were picked out and reweighed.

Burn off = 15%
Calculated " " = 12%

This was considered to be good agreement especially as material would be lost during handling.)

#3c Charcoal							
Jul. 5	100-150	0	1.000	51.2			
		2	1.003	838	.0394	.0387	6.41
		5	1.003		.0355	.0349	5.80
		10		838	.0320	.0315	5.25
		20		838	.0325	.0320	5.35
		30		838	.0326	.0321	5.41
			1.003	51.7			
Jul. 10	100-150	0	1.000	50.5			
		2	1.020	887	.1288	.1210	20.1
		5			.1151	.1088	18.2
		10	1.016	887	.1052	.0999	16.8
		20	1.016		.0988	.0941	16.1
		30		884	.0941	.0899	15.7
			.990	51.3			
Jul. 11	100-150	0	1.000	51.1			
		2	1.053	915	.3268	.2809	51.1
		5	1.050		.2760	.2425	44.8
		10		914	.2437	.2172	41.0
		20	1.041		.2080	.1884	36.9
		30		913	.2014	.1830	37.2
			1.002	53.3			
Jul. 13	100-150	0	1.002	927	51.9		
		2	1.059		.3116	.2696	55.5
		5	1.053	926	.2908	.2539	53.2
		10		926	.2549	.2261	48.6
		20	1.053	926	.2431	.2167	48.9
		30	1.050	926	.2165	.1953	46.2
		40	1.050	926	.2217	.1996	49.5
		50	1.048	926	.2081	.1885	49.2
			1.002	52.7			
Jul. 23	100-150	0	.984	873	53.0		
		2		875	.0960	.0916	15.4
		5	1.000	875	.0830	.0797	13.4
		10	.993	875	.0714	.0689	11.7
		20	.993	876	.0702	.0678	11.6
		30			.0737	.0711	12.3
		-	.976	53.2			
Jul. 24	100-150	0	.981	898	55.1		
		2	1.000	900	.1582	.1466	26.2
		5	1.000		.1395	.1304	23.5
		10		900	.1217	.1148	20.9
		20	1.003	900	.1175	.1110	20.6
		30		898	.1198	.1130	21.5
		-	.981	53.6			
Jul. 26	100-150	0	1.003	52.2			
		2	1.062	927	.3583	.3039	54.9
		5	1.068	927	.3339	.2861	52.5
		10	1.062	927	.3255	.2799	52.7
		20	1.060	927	.3053	.2649	52.6
		30		927	.2798	.2455	51.3
		-	1.003	47.8			

Charcoal									
Sep. 20	48-65	0	1,003	866	52.7				
		2				.0477	.0466	7.98	
		5	1,011	866		.0337	.0332	5.69	
		10				.0385	.0378	6.50	
		20	1,012	866		.0433	.0422	7.31	
		30				.0433	.0422	7.36	
			1,003		53.2				
Sep. 21	48-65	0	.996	917	50.0				
		2	1,023	917		.1358	.1271	21.0	
		5		917		.1337	.1253	20.8	
		10	1,028	917		.1275	.1198	20.1	
		20		917		.1396	.1305	22.4	
		30		917		.1358	.1271	22.3	
			.994		50.7				
Sep. 22	48-65	0	.998		53.0				
		2	1,051	939		.3148	.2720	49.4	
		5	1,054	939		.3033	.2634	48.6	
		10	1,051	939		.2697	.2377	44.9	
		22		939		.2207	.1988	39.5	
		30				.2312	.2072	42.5	
			.998		52.1				
Oct. 4	48-65	0	.981		54.4				
		2				.0706	.0681	11.63	
		5	1,000	875		.0676	.0654	11.19	
		10	1,000			.0619	.0601	10.34	
		20	1,000			.0556	.0541	9.41	
		30				.0539	.0525	9.22	
Oct. 5	48-65	0	.996		52.2				
		2				.1089	.1032	18.1	
		5	1,012			.0889	.0851	15.0	
		10		891		.0787	.0757	13.5	
		20	1,012			.0755	.0727	13.1	
		30	1,013			.0736	.0710	13.0	
		-	1,004		53.1				
Oct. 6	48-65	0	.996		52.4				
		2				.2757	.2423	44.3	
		5	1,059			.2477	.2204	40.8	
		10	1,036	932		.2142	.1935	36.6	
		20	1,030			.1948	.1775	34.8	
		30	1,026			.1840	.1685	34.2	
		-	.981		53.7				

OVERALL ACTIVATION ENERGY PLOT DATA

Sample #	R x 10 ⁻⁴ per min	log(R · 10 ⁴) (y)	Temp. °C	Temp. K	(x) · 10 ⁴ T°K	x ²	xy	a	b
3a	60.5	1.782	979	1252	7.99	63.84	14.238	12.76	-1.37
	46.4	1.667	962	1235	8.10	65.61	13.503		
	21.9	1.340	923	1196	8.36	69.89	11.202		
	19.7	1.295	915	1188	8.42	70.90	10.904		
	9.5	0.978	895	1168	8.56	73.27	8.372		
	8.0	0.903	880	1153	8.67	75.18	7.829		
	3.5	0.544	855	1128	8.87	78.68	4.825		
3b	40.5	1.608	939	1212	8.25	68.06	13.266	12.55	-1.33
	34.4	1.537	932	1205	8.30	68.89	12.757		
	22.1	1.344	947	1190	8.40	70.56	11.290		
	13.0	1.114	891	1164	8.59	73.79	9.597		
	9.1	0.959	875	1148	8.71	75.86	8.344		
	7.3	0.863	866	1139	8.78	77.09	7.577		
3c	52.0	1.716	927	1200	8.33	69.39	14.294	14.51	-1.54
	49.0	1.690	926	1199	8.34	69.56	14.095		
	37.0	1.568	914	1187	8.42	70.90	13.203		
	21.0	1.322	900	1173	8.53	72.76	11.277		
	15.8	1.199	887	1160	8.62	74.30	10.335		
	11.6	1.065	875	1148	8.71	75.86	9.276		
	5.1	0.708	838	1111	9.00	81.00	6.372		

Hence activation energies in kcal/gm. mole are:

Charcoal No.	Activation Energy
3a	63
3b	61
3c	71

The linear portions of the rate curves were used as the characteristic reaction rates at their corresponding temperatures. The results were tabulated and an activation energy plot drawn, the best line being obtained by the method of least mean squares as described for Series B (page 94). The working equation is:-

$$(\log (R \times 10^4)) = b \left(\frac{10^4}{T} \right) + a$$

Series B1

Description of Experiment

Jan., 24th

1/2 gm No. 3a charcoal and 2 gm aluminum were evacuated for 3 hours at temperature of experiment. The flow rate was varied with a short interval between the runs.

Time (mins.)	Flow rate cc/sec.	Temp °C	Units CO	Units CO ₂	% CO ₂	% CO
Calibrate	1.02(He)		368 x 100	2158 x 20	100	100
M(bypassed mixture)	3.97	892		2240 x 10	51.90	
3.35 - 2.37	3.88	"	590 x 1	2125 x 10	49.14	1.60
- 2.40	3.94	"	668 x 1	2200 x 10	50.97	1.82
- 2.45	3.88	"	700 x 1	2200 x 10	50.86	1.90
- 3.50	3.91	"	627 x 1	2160 x 10	49.84	1.70
M	3.88	"		2240 x 10	51.47	
M	2.66	"		2097 x 10	47.99	
3.14 - .16	2.67	"	825 x 1	2080 x 10	47.49	2.21
.19	2.72	"	812 x 1	2110 x 10	48.06	2.18
.24	2.70	"	767 x 1	2070 x 10	47.05	2.05
.29	2.72	"	755 x 1	2070 x 10	46.94	2.01
M	2.66	"		2182 x 10	49.37	
M	1.43	"		2326 x 10	52.39	
3.52 - .54	1.47	"	744 x 2	2140 x 10	48.07	3.94
.57	1.47	"	673 x 2	2150 x 10	48.21	3.56
- 4.00	1.47	"	695 x 2	2155 x 10	48.21	3.67
- 4.07	1.47	"	665 x 2	2160 x 10	48.21	3.50
M	1.43			2280 x 10	50.85	
M	1.014	902		2470 x 10	52.94	
5.51 - .53	1.040	"	255 x 10	2125 x 10	45.44	6.46
- .56	1.041	"	270 x 10	2176 x 10	46.50	6.84
- 6.01	1.046	"	244 x 10	2175 x 10	46.38	6.16
- 6.06		"	232 x 10	2170 x 10	46.27	5.86
M	1.010	"		2423 x 10	51.66	
Calibrate	0.885(He)		396 x 100	2345 x 20	100	100

Derived Results

Jan., 24th

		Basis 1 sec		All volumes in cc					
Average flow rate in	Average CO ₂ in	CO ₂ in He in	Flow rate out	CO ₂ out	CO out	CO ₂ + 1/2 CO out	Temp °C	gm. C gasified during run	
3.93	2.03	1.90	1.07	3.90	1.96	.069	1.05	892	.02
2.66	1.29	1.37	0.94	2.70	1.28	.057	.96	892	.01
1.43	.738	.692	1.07	1.47	0.708	.054	1.06	892	.01
1.012	.529	.483	1.10	1.042	.481	.066	1.06	902	.02

W/F	gm. C cc He/sec	gm. C gasified 1 gm. C/ sec. 10 ⁴	Correction*for p.p. of CO ₂ to 50%	gm. C gasified/ gm. C/ min x 10 ⁴
.263		.370	.364	21.84
.350		.318	.324	19.04
.679		.308	.305	18.30
.952 +		.340	.335	20.10

+ Corrected to 892° C using series A results:

- C gasified = 12%

* Using B2 results

Series B2

Description of Experiment

Jan. 26th

1/2 gm No. 3a charcoal and 2 gm aluminum were evacuated for 3 hours at temperature of experiment. The partial pressure of carbon dioxide in the inlet flow was varied.

Time (mins)	Flow rate cc/sec.	Temp °C	Units CO	Units CO ₂	% CO ₂	% CO	Avg CO ₂	Avg CO
Calibrate	1.081(He)	899	360 x 100	2030 x 20	100	100		
M	1.461	899		2690 x 10	66.03			
1.48 - 1.53	1.480	"	620 x 2	2375 x 10	58.30	3.444		
1.58	1.488	"	618 x 2	2280 x 10	55.96	3.433	57.11	3.496
2.03	1.488	"	650 x 2	2325 x 10	57.07	3.611		
M	1.454	"		2397 x 10	58.84			
M	1.454	"			100			
2.22 - 2.27	1.471	"	170 x 10	1940 x 20	95.24	4.722		
2.29	1.471	"	752 x 2	1940 x 20	95.24	4.178	95.40	4.439
2.32		896	795 x 2	1950 x 20	95.73	4.417		
M	1.436				100			
M	1.461	896		1570 x 10	38.54			
2.46 - 2.50	1.444	895	410 x 2	1440 x 10	35.35	2.278		
2.55	1.444	"	450 x 2	1444 x 10	35.44	2.500	35.22	2.429
3.00		"	450 x 2	1420 x 10	34.86	2.500		
M	1.397	"		1477 x 10	36.25			
M	1.453	896		1010 x 10	24.79			
3.53 - 3.57	1.470	"	360 x 2	1000 x 10	24.55	2.000		
4.03	1.461	"	735 x 1	1010 x 10	24.79	2.042	24.49	2.053
4.08		"	762 x 1	983 x 10	24.13	2.117		
M	1.438	"		1012 x 10	24.84			
Calibrate			360 x 100	2044 x 20	100	100		

Average flow rate in	Average CO ₂ in	He in	CO ₂ in He	Flow rate out	CO ₂ out	CO out	CO ₂ + 1/2 CO out He	Temp °C
1.457	.910	0.547	1.66	1.485	.848	.052	1.60	899
1.445	1.445	0		1.471	1.403	.065		896
1.429	.534	.895	.597	1.444	.509	.035	.589	895
1.446	.359	1.087	.330	1.466	.359	.030	.344	896

P.P. CO ₂	gm.C gasified/ gm.C/sec x 10 ⁴
.624	.279
1.000	.356
.374	.200
.248	.175

Run B3 1/2 gm #2 Cand 2 gm Al₂O₃. 3 hr. evacuation & 1 hr. between runs.

Time (mins)	Flow rate cc/sec	Temp°C	% CO ₂	% CO	Average CO ₂ % out	Average CO % out
0	1.421		51.70			
5	1.440	888	50.00	2.740		
10	1.436	888	49.40	2.795	49.72	2.744
15	1.436	888	49.75	2.696		
-	1.411		52.30			
0	1.389		54.28			
5	1.437	924	46.93	5.994		
10	1.437	924	47.87	6.199	47.40	6.131
15	1.445	924	-	6.199		
-	1.396		52.31			
0	1.406		53.78			
5	1.412	866	51.17	1.695		
10	1.412	866	51.29	2.006	51.32	1.737
15	1.412	866	51.49	1.511		
-	1.396		52.66			
0	1.412		52.33			
5	1.437	918	48.16	5.364		
10	1.429	918	49.02	5.273	48.26	5.263
15	1.437	918	47.60	5.152		
-	1.389		50.74			

Derived Data

Basis: cc/sec

Flow rate in	CO ₂ in	Flow rate out	CO ₂ out	CO out	CO ₂ + 1/2 CO out	Temp °K	gm.C gasified during run	gm.C gasified/ gm.C/sec x 10 ⁴
1.416	.7363	1.437	.7145	.0394	.7342	1161	.010	.213
1.401	.7456	1.412	.7246	.0245	.7369	1139	.006	.134
1.393	.7425	1.440	.6826	.0883	.7268	1197	.021	.499
1.400	.7215	1.434	.6920	.0755	.7298	1191	.018	.436
$\frac{10^4}{T}$	gm.C gasified corrected to 50% CO ₂	gm. gasified/ gm.C/min R x 10 ⁴	log (R x 10 ⁴)					
8.61	.208	12.5	1.097					
8.78	.125	7.5	0.875					
8.35	.490	29.4	1.468					
8.40	.433	26.0	1.415					

Run B4 1/2 gm #4 C and 2 gm Al₂O₃. Note slightly greater depth of bed.

Time (mins)	Flow rate cc/sec	Temp°C	% CO ₂	% CO	Average CO ₂ % out	Average CO % out
0	1.445		52.79			
5	1.445	894	53.23	2.184		
10	1.453	894	52.18	2.289	52.75	2.258
15	1.453	894	52.84	2.300		
-	1.438		52.11			
0	1.421		54.52			
5	1.437	871	52.85	1.368		
10	1.429	871	53.09	1.184	52.26	1.216
15	1.437	871	50.83	1.095		
-	1.421		55.11			
0	1.437		53.03			
5	1.470	920	51.51	4.211		
10	1.479	922	50.81	4.632		
15	1.470	927	49.51	5.000		
-	1.437		54.49			
0	1.429		53.65			
5	1.471	917	51.87	3.711		
10	1.461	917	51.02	3.879	51.30	3.916
15	1.471	917	51.02	4.158		
-	1.437		54.10			

Derived Data

Basis: cc/sec

Flow rate in	CO ₂ in	Flow rate out	CO ₂ out	CO out	CO ₂ + 1/2 CO out	Temp °K	gm.C gasified during run	gm.C gasified/ gm.C/sec x 10 ⁴
1.442	.7563	1.450	.7649	.0327	.7814	1167	.008	.175
1.421	.7773	1.434	.7494	.0174	.7581	1144	.004	.095
1.437	.7725	1.470	.7572	.0619	.7882	1196	.019	.346
		1.479	.7515	.0685	.7858		.019	.382
		1.470	.7278	.0735	.7645		.019	.410
1.431	.7710	1.467	.7526	.0574	.7813	1190	.014	.334
$\frac{10^4}{T}$	gm.C gasified corrected to 50% CO ₂	gm. gasified/ gm.C/min R x 10 ⁴	log (R x 10 ⁴)					
8.57	.168	10.1	1.004					
8.74	.081	4.9	0.690					
8.36	.368	22.1	1.344					
8.40	.324	19.4	1.288					

Run B5 1/2 gm # 1aC and 2 gm Al₂O₃.

Time (mins)	Flow rate cc/sec	Temp°C	% CO ₂	% CO	Average CO ₂ out	Average CO out
0	1.445		50.32			
5	1.461	904	48.29	3.667		
10	1.471	904	48.44	3.694	47.53	3.593
15	1.461	904	45.85	3.417		
-	1.438		50.71			
0	1.429		52.58			
5	1.445	879	50.55	2.192		
10	1.431	879	49.12	2.164	50.55	2.155
15	1.437	879	52.06	2.110		
-	1.429		51.86			
0	1.429		55.19			
5	1.471	939	48.58	7.398		
10	1.480	939	48.58	8.130	48.46	8.022
15	1.480	939	48.21	8.537		
-	1.421		55.90			
0	1.421		54.91			
5	1.471	927	49.53	5.876		
10	1.463	927	48.95	5.687	49.61	5.795
15	1.463	927	50.35	5.822		
-	1.429		52.45			

Derived Data

Basis: cc/sec

Flow rate in	CO ₂ in	Flow rate out	CO ₂ out	CO out	CO ₂ + 1/2 CO out	Temp °K	gm. C gasified during run	gm. C gasified/ gm. C/sec x 10 ⁴
1.442	.7285	1.464	.6958	.0526	.7221	1174	.013	.285
1.429	.7462	1.438	.7269	.0310	.7424	1152	.007	.172
1.425	.7916	1.477	.7158	.1185	.7751	1212	.029	.683
1.425	.7649	1.466	.7273	.0850	.7698	1200	.021	.506
10 ⁴ T	gm. C gasified corrected to 50% CO ₂	gm. gasified/ gm. C/min R x 10 ⁴	log (R x 10 ⁴)					
8.52	.284	17.0	1.230					
8.68	.166	10.0	1.000					
8.25	.668	40.1	1.603					
8.33	.497	29.8	1.474					

Run B6 1/2 gm #1 C and 2 gm Al₂O₃.

Time (mins)	Flow rate cc/sec	Temp°C	% CO ₂	% CO	Average CO ₂ out	Average CO out
0	1.479		48.33			
5	1.506	894	46.90	4.330		
10	1.506	894	44.87	4.604	44.64	4.516
15	1.516	894	46.78	4.615		
-	1.479		50.24			
0	1.471		51.54			
5	1.488	877	48.90	2.826		
10	1.479	877	48.83	2.961	47.93	2.844
15	1.496	877	46.06	2.744		
-	1.461		51.66			
0	1.461		42.09			
5	1.524	936	42.72	8.602		
10	1.532	936	42.81	8.602	42.55	8.781
15	1.532	936	42.11	9.139		
-	1.461		51.14			
0	1.452		49.44			
5	1.497	914	45.28	6.149		
10	1.506	914	6.256	6.256	45.28	6.411
15	1.516	914	45.28	6.828		
-	1.461		51.01			

Derived Data

Basis: cc/sec

Flow rate in	CO ₂ in	Flow rate out	CO ₂ out	CO out	CO ₂ + 1/2 CO out	Temp °K	gm. C gasified during run	gm. C gasified/ gm. C/sec x 10 ⁴
1.479	.7290	1.509	.6736	.0681	.7076	1167	.016	.371
1.466	.7565	1.488	.7132	.0423	.7344	1150	.010	.237
1.461	.7323	1.529	.6506	.1343	.7178	1209	.032	.781
1.457	.7319	1.506	.6819	.0965	.7302	1187	.023	.601
10 ⁴ T	gm. C gasified corrected to 50% CO ₂	gm. gasified/ gm. C/min R x 10 ⁴	log (R x 10 ⁴)					
8.57	.374	22.4	1.350					
8.70	.233	14.0	1.146					
8.27	.781	46.9	1.671					
8.42	.601	36.1	1.558					

Arrhenius Plot

The method of least mean squares was used to obtain the "best" straight line. It was realized that for such a small number of points, this method does not have too much significance other than being an arbitrary method for selecting the best line. Further, it has been assumed that the errors in $\frac{1}{T}$ were small compared with those in $\log R$ and this simplified the calculation.

Thus $y = a + bx$ was fitted

$$\text{where } x = \frac{10^4}{T}$$

$$y = \log(R \cdot 10^4)$$

a, b constants

$$\left. \begin{aligned} b &= \frac{\langle xy \rangle - \frac{\langle x \rangle \langle y \rangle}{n}}{\langle xx \rangle - \frac{\langle x \rangle^2}{n}} \\ a &= \bar{y} - b\bar{x} \end{aligned} \right\} \text{Using the Gauss nomenclature}$$

Calculations

Carbon #	$\frac{10^4}{x} = \frac{1}{T}$	$y = \log v$	$(10^4 R)$	x^2	xy
2	8.61	1.097		74.13	9.445
	8.78	0.875		77.09	7.683
	8.35	1.168		69.72	12.258
	8.40	1.415		70.56	11.886
	8.52	1.230		72.59	10.480
1	8.68	1.000		75.34	8.680
	8.25	1.603		68.06	13.225
	8.33	1.474		69.39	12.278
67.92	10.162			576.88	85.935

$$b = \frac{(xy) - (x)(y)/n}{(xx) - (x)^2/n} = \frac{85.935 - (67.92)(10.162)/6}{576.88 - (67.92)^2/6}$$

$$= \frac{-0.340}{0.24} = -1.417$$

$$a = \frac{10.162}{8} + 1.417 \cdot \frac{67.92}{8} = 13.30$$

Carbon #	x	y	x^2	xy	
4	8.57	1.004	73.44	8.604	a = 15.94; b = -1.744
	8.74	0.690	76.39	6.031	
	8.36	1.344	69.89	11.236	
	8.40	1.288	70.56	10.819	
1	8.57	1.350	73.44	11.570	a = 12.30; b = -1.28
	8.70	1.146	75.69	9.970	
	8.27	1.671	68.39	13.819	
	8.42	1.558	70.90	13.118	

Hence activation energy for

#1	58.5 kcal/mole
#2	64.7 kcal/mole
#3a	64.7 kcal/mole
#4	79.8 kcal/mole

Series C

Description of Experiment

1/2 gm No. 3a charcoal and 2 gm alundum. The partial pressure of carbon dioxide was varied at two temperatures.

Time (min)	Flow rate cc/sec.	Temp °C	Units CO	Units CO ₂	% CO ₂	% CO	Avg CO ₂ % in	Avg CO ₂ % out	Avg CO % out
Apr. 4th			380x100	1993x20	100	100			
M	1.390	883	-	3000x10	75.26		75.68	70.83	2.355
3.39-3.44	1.396	883	925x1	2870x10	72.00	2.434			
3.47	1.411	"	900x1	2900x10	72.75	2.368			
3.50	1.411	"	860x1	2700x10	67.74	2.263			
M	1.404	"	-	3033x10	76.09				
M	1.420	"	-	2228x10	50.51		50.97	49.95	2.182
4.08-4.13	1.437	"	805x1	2150x10	48.74	2.164			
4.15	1.437	"	820x1	2240x10	50.78	2.204			
4.19	1.429	"	810x1	2220x10	50.33	2.177			
M	1.411	"	-	2268x10	51.42				
M	1.437	"	-	1610x10	33.29		32.11	30.18	1.700
4.35-4.40	1.429	"	630x1	1495x10	30.91	1.726			
4.44	1.429	"	607x1	1462x10	30.23	1.663			
4.46	1.429	"	625x1	1422x10	29.40	1.712			
M	1.437	"	-	1496x10	30.93				
Calibration			365x100	2418x20	100	100			
April 5th			390x100	2193x20	100	100			
M	1.454	912	-	3140x10	71.59		72.82	69.95	4.419
1.51-1.55	1.480		150x10	3140x10	71.59	3.846			
1.59	1.497	909	193x10	3032x10	69.13	4.949			
2.03	1.497	912	174x10	3032x10	69.13	4.462			
M	1.462	"	-	1624x20	74.05				
M	1.429	912	-	2255x10	49.64		51.68	49.95	3.937
2.16-2.20	1.444	"	160x10	2210x10	48.65	4.082			
2.24	1.444	"	160x10	2298x10	50.58	4.082			
2.28	1.436	"	143x10	2300x10	50.63	3.648			
M	1.421	"	-	2440x10	53.71				
M	1.462	909	-	1328x10	28.26		29.03	27.47	2.290
2.45-2.49	1.470	"	433x2	1280x10	27.23	2.192			
2.52	1.480	"	484x2	1315x10	27.98	2.451			
2.56	1.470	"	440x2	1278x10	27.19	2.228			
M	1.462	"	-	1400x10	29.79				
			395x100	2350x20	100	100			

Description of Experiment

1/2 gm No. 1 charcoal and 2 gm aluminum. The partial pressure of carbon dioxide was varied at two temperatures.

Time(min)	Flow rate cc/sec.	Temp °C	Units CO	Units CO ₂	% CO ₂	% CO	Avgc CO ₂ % in	Avgc CO ₂ % out	Avgc CO % out
9th April			370x100	2070x20	100	100			
M	1.453	-	-	2750x10	66.43		66.97	62.78	4.463
2.40-2.44	1.488	884	755x2	2612x10	63.09	4.081			
2.48	1.488	"	870x2	2645x10	63.89	4.703			
2.51	1.488	"	852x2	2540x10	61.35	4.605			
M	1.453	-	-	2795x10	67.51				
M	1.429	884	-	2087x10	49.69		49.92	48.04	4.009
3.45-3.49	1.461	"	700x2	1986x10	47.29	3.784			
3.54	1.453	"	740x2	2040x10	48.57	4.000			
3.58	1.453	"	785x2	2027x10	48.26	4.243			
M	1.429	-	-	2106x10	50.14				
M	1.458	"	-	1235x10	28.99		29.23	27.09	3.220
4.13-4.17	1.462	"	585x2	1170x10	27.46	3.162			
4.21	1.470	"	580x2	1122x10	26.34	3.135			
4.25	1.458	"	622x2	1170x10	27.46	3.362			
M	1.444	"	-	1255x10	29.46				
Calib.			370x100	2130x20	100	100			
10th April			366x100	2065x20	100	100			
M	1.438	-	-	2982x10	72.20		72.64	64.92	7.359
1.43-1.47	1.480	910	263x10	2665x10	64.53	7.186			
1.50	1.488	"	272x10	2669x10	64.62	7.432			
1.53	1.488	"	273x10	2710x10	65.62	7.459			
M	1.429	"	-	3018x10	73.08				
M	1.420	"	-	2095x10	48.70		48.88	44.09	6.275
2.08-2.12	1.452	"	238x10	1915x10	44.51	6.214			
2.16	1.461	"	243x10	1885x10	43.82	6.345			
2.20	1.470	"	240x10	1890x10	43.93	6.266			
M	1.428	-	-	2110x10	49.05				
M	1.453	-	-	1338x10	29.91		29.36	25.58	5.817
2.45-2.49	1.480	914	225x10	1162x10	25.97	5.625			
2.53	1.480	"	233x10	1178x10	26.33	5.825			
2.58	1.480	"	240x10	1094x10	24.45	6.000			
M	1.428	-	-	1280x10	28.61				
Calib.			400x100	2237x20	100	100			

Description of Experiment

1/2 gm No. 4 charcoal and 2 gm aluminum. The partial pressure of carbon dioxide was varied at two temperatures.

Time(min)	Flow rate cc/sec.	Temp °C	Units CO	Units CO ₂	% CO ₂	% CO	Avgc CO ₂ % in	Avgc CO ₂ % out	Avgc CO % out
12th April			340x100	2038x20	100	100			
M	1.438	-	-	2785x10	67.79		68.71	66.80	2.574
1.56-2.00	1.444	891	430x2	2746x10	66.85	2.529			
2.05	1.461	"	443x2	2748x10	66.89	2.606			
2.09	1.444	"	440x2	2738x10	66.65	2.588			
M	1.438	-	-	2860x10	69.62				
M	1.438	892	-	1865x10	45.40		45.83	44.61	2.098
2.27-2.31	1.444	"	364x2	1837x10	44.72	2.056			
2.35	1.453	"	350x2	1800x10	43.82	1.977			
2.39	1.444	"	400x2	1860x10	45.28	2.260			
M	1.429	-	-	1900x10	46.25				
M	1.412	892	-	1240x10	29.95		30.00	27.95	1.592
2.55-2.59	1.420	"	300x2	1143x10	27.61	1.639			
3.04	1.420	"	294x2	1130x10	27.29	1.607			
3.07	1.412	"	280x2	1198x10	28.94	1.530			
M	1.404	-	-	1244x10	30.05				
Calib.			366x100	2070x20	100	100			
April 13th			365x100	2110x20	100	100			
M	1.444	-	-	3092x10	73.27		74.31	69.48	5.278
2.01-2.05	1.480	922	200x10	2930x10	69.43	5.479			
2.09	1.480	"	190x10	2892x10	68.53	5.205			
2.13	1.489	922	188x10	2974x10	70.47	5.151			
M	1.444	-	-	3180x10	75.36				
M	1.444	922	-	1896x10	44.22		44.68	42.25	3.580
2.27-2.32	1.461	921	130x10	1808x10	42.16	3.439			
2.35	1.461	921	140x10	1822x10	42.49	3.704			
2.38	1.461	"	136x10	1805x10	42.09	3.598			
M	1.444	-	-	1935x10	45.13				
M	1.480	922	-	1212x10	27.82		28.56	26.32	2.949
2.49-2.54	1.489	"	120x10	1130x10	25.94	3.077			
2.58	1.498	"	105x10	1156x10	26.54	2.692			
3.00	1.489	"	120x10	1153x10	26.47	3.077			
M	1.480	-	-	1276x10	29.29				
Calib.			390x100	2178x20	100	100			

Description of Experiment

1/2 gm No. 1 charcoal and 2 gm alundum. CO₂ and CO in inlet flow only.

Time (min)	Flow cc/sec	Temp °C	Units		%		Corrected %	
			CO	CO ₂	CO ₂	CO	CO ₂	CO
Calibrate			370x100	2201x20	100	100		
M	1.445	939	1210x10	2846x10	64.65	32.70	66.40	33.60
1.55-2.00	1.479	"	710x20	1359x20	61.74	38.38	61.66	38.34
	2.05	1.488	705x20	1313x20	59.65	38.11	61.01	38.99
M	1.445		626x20	1451x20	65.92	33.84	66.07	33.93
M	1.420	938	836x10	3355x10	75.46	22.66	76.90	23.10
2.17-2.22	1.453	"	1025x10	3098x10	69.68	27.77	71.50	28.50
	2.27	1.453	1039x10	3117x10	70.10	28.15	71.34	28.66
M	1.420		820x10	3248x10	73.05	22.22	76.67	23.33
M	1.437		831x20	2275x10	50.71	45.16	52.89	47.11
2.40-2.45	1.453	"	925x20	2237x10	49.86	50.27	49.79	50.21
	2.50	1.437	893x20	2196x10	48.95	48.53	50.21	49.79
M	1.381		821x20	2306x10	51.40	44.62	53.53	46.46
M	1.397		1192x20	1520x10	33.53	64.78	34.10	65.90
3.03-3.08	1.412	"	1225x20	1466x10	32.34	66.57	32.69	67.31
	3.13	1.420	1226x20	1465x10	32.32	66.63	32.66	67.34
M	1.404		1198x20	1563x10	34.48	65.10	34.62	65.38
Calibrate			367x100	2266x20	100	100		

Time (min)	Flow cc/sec	Temp °C	Units		%		Corrected %	
			CO	CO ₂	CO ₂	CO	CO ₂	CO
Calibrate			365x100	2150x20	100	100		
M	1.429	1011	1044x20	1674x10	38.93	56.13	40.95	59.05
1.50-1.55	1.524	"	1200x20	1408x10	32.74	64.52	33.66	66.34
	2.00	1.524	1200x20	1404x10	32.65	64.52	33.60	66.40
M	1.437		1052x20	1751x10	40.72	56.56	41.86	58.14
M	1.515	1012	244x100	1400x10	32.44	65.95	32.97	67.03
2.27-2.32	1.572	"	287x100	1045x10	24.21	77.57	23.79	76.21
	2.37	1.558	275x100	1080x10	25.02	74.32	25.19	74.81
M	1.471		240x100	1400x10	32.44	64.86	33.34	66.66
M	1.437		600x20	1459x20	67.33	31.91	67.85	32.15
2.47-2.52	1.592	"	906x20	1070x20	49.38	48.19	50.61	49.39
	2.57	1.592	921x20	1057x20	48.78	48.99	49.89	50.11
M	1.429		610x20	1526x20	70.42	32.45	68.46	31.54
M	1.462	"	300x20	1863x20	85.62	15.79	84.44	15.56
3.13-3.18	1.667	"	740x20	1282x20	58.92	38.95	60.20	39.80
	3.23	1.656	720x20	1300x20	59.74	37.89	61.19	38.81
M	1.445		260x20	1860x20	85.48	13.68	86.20	13.80
Calibrate			380x100	2176x20				

Description of Experiment

1/2 gm No. 3a C and 2 gm aluminum. CO₂ and CO in inlet flow only.

Time (min)	Flow cc/sec	Temp °C	Units		%		Corrected %	
			CO	CO ₂	CO ₂	CO	CO ₂	CO
Calibrate			350x100	2096x20	100	100		
M	1.344	932	908x10	3095x10	73.83	25.94	74.00	26.00
1.35-1.40	1.397	"	1062x10	2928x10	69.85	30.34	69.72	30.28
1.45	1.397	"	1096x10	2938x10	70.09	31.31	69.12	30.88
1.50	1.397	"	1047x10	2910x10	69.42	29.91	69.89	30.11
M	1.366		882x10	3012x10	71.85	25.20	74.03	25.97
M	1.404	934	490x10	1900x20	89.33	13.76	86.65	13.35
2.10-2.15	1.445	"	651x10	1760x20	82.75	18.29	81.90	18.10
2.20	1.453	"	707x10	1793x20	84.30	19.86	80.93	19.07
2.25	1.453	"	666x10	1775x20	83.45	18.71	81.69	18.31
M	1.420		468x10	1970x20	92.62	13.15	87.57	12.43
M	1.437	936	986x20	1830x10	42.40	54.48	43.77	56.23
2.35-2.40	1.453	"	1022x20	1835x10	42.52	56.46	42.96	57.04
2.45	1.453	"	1066x20	1788x10	41.43	58.90	41.29	58.71
2.50	1.453	"	1050x20	1810x10	41.94	58.01	41.96	58.04
M	1.437		970x20	1840x10	42.63	53.59	44.30	55.70
Calibrate			362x100	2158x20	100	100		
Time (min)	Flow cc/sec	Temp °C	Units		%		Corrected %	
			CO	CO ₂	CO ₂	CO	CO ₂	CO
Calibrate			366x100	2161x20	100	100		
M	1.445	998	885x10	3240x10	74.97	24.18	75.61	24.39
1.51-1.57	1.582	"	763x20	1267x20	58.63	41.69	58.44	41.56
2.01	1.582	"	741x20	1364x20	63.12	40.49	60.92	39.08
M	1.445	"	851x10	3343x10	77.35	23.25	76.89	23.11
M	1.412	"	586x20	1507x20	67.55	30.84	68.66	31.34
2.16-2.20	1.543	"	805x20	1234x20	55.31	42.37	56.62	43.38
2.23	1.543	"	822x20	1232x20	55.22	43.26	56.07	43.93
M	1.429	"	584x20	1584x20	71.00	30.74	69.79	30.21
M	1.471	999	290x100	1424x10	30.04	71.25	29.66	70.34
3.05-3.10	1.524	"	296x100	1259x10	26.56	72.73	26.75	73.25
3.15	1.506	"	282x100	1235x10	26.05	69.29	27.32	72.68
M	1.445	"	280x100	1470x10	31.01	68.80	31.07	68.93
Calibrate			407x100	2370x20				

Description of Experiment

1/2 gm No. 4 charcoal and 2 gm aluminum.

Time (min)	Flow cc/sec	Temp °C	Units		%		Corrected %	
			CO	CO ₂	CO ₂	CO	CO ₂	CO
Calibrate			378x100	2260x20	100	100		
M	1.420		935x20	1100x20	48.67	49.47	49.59	50.41
1.45-1.50	1.553	1004	1195x20	750x20	33.19	63.23	34.42	65.58
	1.55	1001	1128x20	788x20	34.87	59.68	36.88	63.12
M	1.397		924x20	1063x20	47.04	48.89	49.04	50.96
M	1.462		674x20	1417x20	62.34	35.29	63.85	36.15
2.10-2.15	1.597	1003	975x20	1072x20	47.16	51.05	48.02	51.98
	2.20	1003	940x20	1140x20	50.15	49.21	50.47	49.53
M	1.453		654x20	1515x20	66.65	34.24	66.06	33.94
M	1.445		450x20	1782x20	77.95	23.44	76.88	23.12
2.35-2.40	1.592	1002	770x20	1324x20	63.47	40.10	61.28	38.72
	2.45	1002	772x20	1390x20	60.80	40.21	60.19	39.81
M	1.420		422x20	1760x20	76.99	21.98	77.79	22.21
M	1.488		277x100	1510x10	32.83	71.95	31.33	68.67
3.00-3.05	1.543	1002	298x100	1150x10	25.00	77.40	24.41	75.59
	3.10	1002	283x100	1246x10	27.09	73.51	26.93	73.07
M	1.471		263x100	-		68.31		68.31
Calibrate			385x100	2300x20	100	100		

Time (min)	Flow cc/sec	Temp °C	Units		%		Corrected %	
			CO	CO ₂	CO ₂	CO	CO ₂	CO
Calibrate			380x100	2188x20	100	100		
M	1.453		514x20	1565x20	71.53	27.05	72.56	27.44
1.28-1.33	1.488	940	623x20	1500x20	68.56	32.79	67.65	32.35
	1.38	941	613x20	1536x20	70.20	32.26	68.51	31.49
M	1.471		535x20	1620x20	74.04	28.16	72.45	27.55
M	1.479		769x10	1808x20	80.61	19.92	80.19	19.81
1.55-2.00	1.488	940	922x10	1755x20	78.24	23.89	76.61	23.39
	2.05	940	908x10	1760x20	78.47	23.52	76.94	23.06
M	1.462		766x10	1872x20	83.46	19.84	80.79	19.21
M	1.471		1076x20	2050x10	44.60	54.89	44.83	55.17
2.20-2.25	1.462	937	1115x20	1988x10	43.26	56.89	43.20	56.80
	2.30	937	1088x20	1981x10	43.10	55.51	43.71	56.29
M	1.429		1092x20	2044x10	44.47	55.71	44.39	55.61
Calibrate			397x100	2352x20	100	100		

APPENDIX B

Effect of External Diffusion

The results of experiment B1 in which the flow rate was varied from 4 to 1 cc/sec over No. 3a charcoal at 892° C but the rate of gasification of the charcoal did not vary implied that external diffusion to and from the particles was not a controlling factor within the range studied.

A calculation to confirm this is given, c.f. Smith (32)

$$\text{At } 900^{\circ}\text{C, the viscosity of helium} = 0.049 \text{ cps} \quad (27)$$

$$\text{carbon monoxide} = 0.046 \text{ cps} \quad (27)$$

$$\text{carbon dioxide} = 0.045 \text{ cps} \quad (20)$$

The viscosity of the mixture will be taken as 0.047 cps.

The particle diameter $d_p = 0.1524 \text{ cm}$.

The mass flow rate at 1.5 cc/sec containing 50% CO_2 and 50% He

$$\text{by volume at 1 at. pressure} = 0.75 \left(\frac{44}{22,400} + \frac{4}{22,400} \right) \text{ gm/sec}$$

$$= 1.608 \times 10^{-3} \text{ gm/sec.}$$

The dia. of the reactor = 1 cm

$$\text{and so the superficial mass velocity } G = \frac{1.608 \times 10^{-3}}{\pi/4} \text{ gm/cm}^2/\text{sec}$$

$$= 2.045 \times 10^{-3} \text{ gm/cm}^2/\text{sec}$$

$$\therefore \text{Reynold's Number} = \frac{d_p G}{\mu} = \frac{0.1524 \times 2.045 \times 10^{-3}}{0.047 \times 10^{-2}}$$

$$= 663$$

$$\therefore j_o = \frac{k_g M_p P_f}{G} \left(\frac{\mu}{e D} \right)^{2/3} = 1.82 \left(\frac{d_p G}{\mu} \right)^{-0.51}$$

Also $r = k_g a(p_i - p_g)$ for CO diffusing from particles

$$\therefore p_i - p_g = \frac{M_m R r}{1.82 a G (d_p G / \mu)^{-0.51} \left(\frac{\mu}{\ell D} \right)^{2/3}}$$

The diffusivity of CO in He and CO₂ may be calculated from Gilliland's equation.

$$D_{AB} = 0.0043 \frac{T^{3/2}}{p_t \left\{ V_A^{1/3} + V_B^{1/3} \right\}^2} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}$$

$\therefore$ where D_{AB} = diffusivity of A in B sq.cm/sec

T = temp °K

M_A, M_B = mol. wts. of A and B

p_t = total pressure atm.

V_A, V_B = molecular volumes of A and B

So for CO in He

$$D_{COHe} = 0.0043 \frac{1165^{3/2}}{1 \{ (14.3)^{1/3} + (30.7)^{1/3} \}^2} \left(\frac{1}{28} + \frac{1}{4} \right)^{1/2}$$

(The molecular volume for hydrogen in the table has been used as sufficiently near the helium value.)

$$\begin{aligned} \therefore D_{COHe} &= \frac{0.0043 \times 39800 \times 0.535}{31} \text{ cm}^2/\text{sec} \\ &= 2.95 \text{ cm}^2/\text{sec} \end{aligned}$$

and for CO in CO₂

$$\begin{aligned} D_{COCO_2} &= \frac{0.0043 \times 39800 \times 0.242}{40.6} \\ &= 1.02 \text{ cm}^2/\text{sec} \end{aligned}$$

A mean diffusion coefficient of 2 cm²/sec will be taken for the mixture.

The density of the gas mixture will be $\frac{22 + 2}{22400}$ gm/cc

$$= 1.07 \times 10^{-3} \text{ gm/cc at S.T.P.}$$

$$= 1.07 \times 10^{-3} \times \frac{273}{1165} = 2.51 \times 10^{-4} \text{ gm/cc}$$

$$\begin{aligned} \text{Then the Schmidt Group } \left(\frac{u}{D} \right) &= \frac{0.047 \times 10^{-2}}{2.51 \times 10^{-4} \times 2} \\ &= .0936 \end{aligned}$$

At the low conversions encountered experimentally, the mean molecular weight $M_m = 24$.

The pressure film factor p_f will be taken as equal to the total pressure = 1 at.

The external area per unit mass of catalyst = 53 sq.cm/gm.

Rate of reaction at 892° (experimentally) = $.33 \times 10^{-4}$
gm carbon/gm carbon/sec.

12 gm carbon correspond to 1 gm mol. CO_2 reacted

$$\therefore r = \frac{.33 \times 10^{-4}}{12} \text{ gm mol. CO}_2/\text{gm carbon/sec.}$$

$$\begin{aligned} \therefore p_i - p_g &= \frac{24 \times 1 \times \left(\frac{.33 \times 10^{-4}}{12} \right)}{1.82 \times 53 \times 2.045 \times 10^{-3} \times (6663)^{-0.51} \left(\begin{array}{c} (.0936) \\ \end{array} \right)^{2/3}} \\ &= \frac{.66 \times 10^{-1} \times .206 \times 2.63}{1.82 \times 53 \times 2.045} \text{ at} \\ &= 2.71 \times 10^{-3} \text{ at} \end{aligned}$$

The percentage of CO in the outgoing gas from this experiment is about 4% by volume

$$\text{i.e. } p_g = 4 \times 10^{-2} \text{ at}$$

1. The first part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation

$$f(x) = \int_0^x f(t) dt + \int_0^x f(t) dt + \dots$$

$$f(x) = \int_0^x f(t) dt + \int_0^x f(t) dt + \dots$$

$$f(x) = \int_0^x f(t) dt + \int_0^x f(t) dt + \dots$$

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$$\left\{ \begin{array}{l} f(x) \\ f(x) \\ f(x) \end{array} \right\} = \left\{ \begin{array}{l} f(x) \\ f(x) \\ f(x) \end{array} \right\} = \left\{ \begin{array}{l} f(x) \\ f(x) \\ f(x) \end{array} \right\}$$

$$f(x) = \int_0^x f(t) dt + \int_0^x f(t) dt + \dots$$

$$f(x) = \int_0^x f(t) dt + \int_0^x f(t) dt + \dots$$

$$f(x) = \int_0^x f(t) dt + \int_0^x f(t) dt + \dots$$

$$f(x) = \int_0^x f(t) dt + \int_0^x f(t) dt + \dots$$

$$f(x) = \int_0^x f(t) dt + \int_0^x f(t) dt + \dots$$

$$f(x) = \int_0^x f(t) dt + \int_0^x f(t) dt + \dots$$

It can thus be seen that the external diffusion resistance may be neglected.

The effect of internal diffusion may now be calculated from the same data.

Effect of Internal Diffusion

Mean pore radius will be taken as 11×10^{-8} cm (see Sec. IV.8)

Treybal (35) gives
$$\lambda = \frac{3.2 \mu}{p} \sqrt{\frac{RT}{2 \pi g_c M}}$$

to determine the mean free path (λ cm) of the gas

where μ = viscosity in poise

p = pressure gm/sq.cm

R = 84780 gm cm/gm mole °K.

T = temp °K.

g_c = 980 gm mass cm/gm force sec²

M = mol. weight

e.g. Helium at 900°C and 1 at

$$\mu = 0.049 \times 10^{-2} \text{ poise}$$

$$p = 1033.2 \text{ gm/sq.cm}$$

$$T = 1173^\circ\text{K.}$$

$$M = 4$$

$$\begin{aligned} \therefore \lambda &= \frac{3.2 \times 0.049 \times 10^{-2}}{1033.2} \sqrt{\frac{84780 \times 1173}{2 \times \pi \times 980 \times 4}} \text{ cm} \\ &= 9630 \text{ \AA} \end{aligned}$$

Similarly for CO₂ $\lambda = 2700 \text{ \AA}$

The mean pore diameter = $22 \text{ \AA} \ll 2700 \text{ \AA}$ and hence Knudsen diffusion would be expected to predominate.

The calculation now follows the pattern of an example in Smith (32) p. 273.

At 892°C $.33 \times 10^{-4}$ gm carbon were gasified per gm #3a carbon per sec. The flow rate varied from 2 cc of CO₂/sec to 0.5 cc of CO₂/sec. but the partial pressure of CO₂ remained constant at 1/2 at.

$$\begin{aligned} \text{The Knudsen Diffusivity } D_k &= 9.7 \times 10^3 (11 \times 10^{-8}) \sqrt{\frac{273 + 892}{44}} \\ &= 5.5 \times 10^{-4} \text{ sq.cm/sec.} \end{aligned}$$

This may be compared with the apparent gas phase diffusion coefficient in the charcoal pores (i.e., all movement along a pore is assumed to occur via the gas phase) as calculated by Habgood & Hanlan (17) from the Van Deemter equation.

This was of the order of 5×10^{-2} sq.cm/sec. at 300°C with slightly higher values at temperatures ranging down to 100°C.

The ratio of the volume of the particle V_p to the external surface area of the particle will be obtained assuming spherical particles of diameter d_p

$$\frac{V_p}{S_x} = \frac{d_p}{6} = \frac{0.1524 \text{ cm}}{6}$$

According to Smith (32), the effectiveness factor E calculated on the basis of a first order reaction is sufficiently accurate as the changes in form of the rate equation have a small effect on the effectiveness factor plot.

Thus assume $E = 0.95$

$$\therefore h = 0.5$$

$$V_g = \text{pore volume/gm} = 0.66 \text{ cc/g for \#3a C}$$

$$k_i = \text{first order rate constant cc/g/sec.}$$



$$\therefore 12 \text{ gm C gasified/sec.} \equiv 22.4 \text{ l CO}_2 \text{ gasified/sec.}$$

$$\therefore 0.33 \times 10^{-4} \text{ gm carbon/gm carbon/sec.}$$

$$\text{corresponds to } \frac{22,400}{12} \times 0.33 \times 10^{-4} \text{ cc/gm/sec} = k_i$$

$$\therefore k_i = 0.0616 \text{ cc/gm/sec. (experimentally)}$$

$$\text{However } h = \frac{2V_p}{S_x} \sqrt{\frac{k_i}{2V_g D_k}}$$

$$\text{i.e. } 0.5 = 2 \left\{ \frac{0.1524}{6} \right\} \left(\frac{10^4}{2 \times 0.66 \times 5.5} \right)^{1/2} k_i^{1/2}$$

$$k_i = \left\{ \frac{3}{2 \times 0.1524} \right\}^2 (7.25 \times 10^{-4}) = 0.07 \text{ cc/gm/sec (calculated)}$$

$$\therefore E = \frac{k_i \text{ experimental}}{k_i \text{ calculated}}$$

$$= \frac{0.06}{0.07} = 0.86$$

It should be noted that this calculation is very sensitive at values of E approaching unity, i.e., if he had been read off the graph in Smith (32) as 0.47 instead of 5, the new E calculated would have been unity.

This calculation plus the fact that the activation energy plots are approximately linear over the range studied will be taken to mean

that porous diffusion has a negligible influence on the reaction rate measured.

Experiment B2 was carried out to see if the reaction was zero order. The rate of gasification was plotted against the partial pressure of carbon dioxide in Fig. 32 and it can be seen that the reaction was not a zero order one. The curve was used to make small corrections for the deviations of the partial pressure of carbon dioxide from 0.5 atm. in the Series B experiments.

VARIATION OF GASIFICATION RATE WITH
P.P. OF CARBON DIOXIDE

896°C

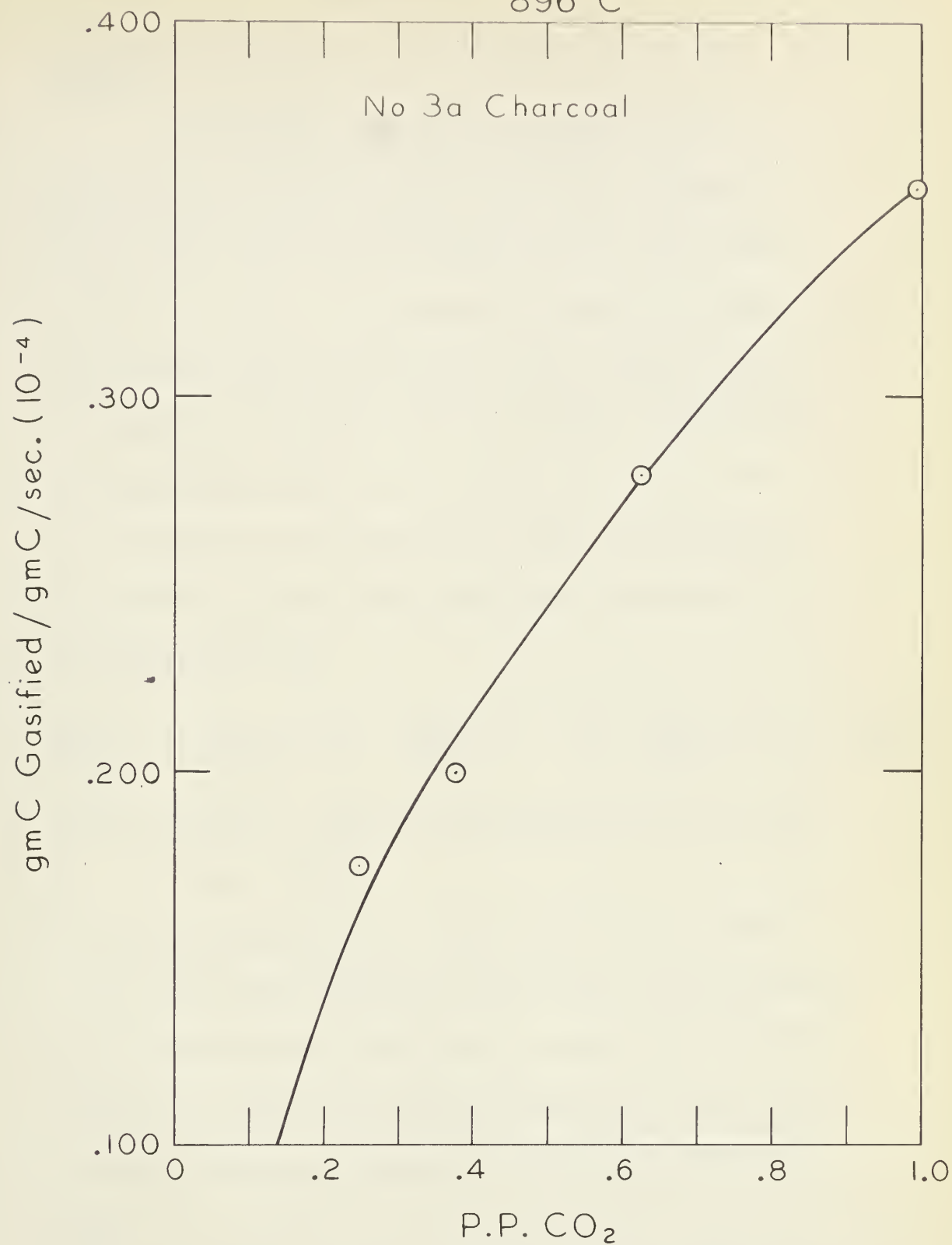


FIGURE 32

APPENDIX C

The Iterative Technique for the Determination of the Reaction Constants

The method of determining the reaction constants briefly described on page 62 is given in detail here. An initial set of values for K_1 at the two lower temperatures was obtained using equation (6) page 49. The data for this equation were obtained from the initial slopes of the gasification rate v. partial pressure of carbon dioxide plots at these lower temperatures. These values were plotted exponentially against temperature and the K_1 values at the temperatures of the experiments, in which carbon monoxide was introduced, read off. These values plus the experimental data were plotted in the form:

$$\left\{ \frac{WK_1}{ax_0} + 1 + \frac{(2b+c)}{(ax_0)} \ln \left(1 - \frac{ax_0}{b} \right) \right\} = K_3 - K_2 \left[2 + \frac{(2b+c)}{(ax_0)} \ln \left(1 - \frac{ax_0}{b} \right) \right]$$

which is equation (5) page 49 rearranged and was abbreviated

$$\text{to } Y = K_3 - K_2X.$$

The slope of this line gives K_2 . These values of K_2 were plotted exponentially against temperature and values of K_2 at the temperatures of the two experiments, in which carbon monoxide was not introduced, read off. New values of K_1 could thus be determined using a similar procedure to that for determining K_2 . The data were plotted in the form:

$$\left\{ 1 - \frac{1}{x_0} \ln \left(1 - \frac{ax_0}{b} \right) - 2(K_2 + 1) \left\{ 1 + \frac{b}{ax_0} \ln \left(1 - \frac{ax_0}{b} \right) \right\} \right\} = \frac{W}{ax_0} \cdot K_1 - K_3$$

which also is equation (5) page 49 rearranged and was abbreviated to

$$Y = K_1 X - K_3$$

The new values of K_1 were plotted exponentially against temperature and the procedure repeated. After very few iterations no further changes were observed.

The tabulated data, calculations and graphs showing the final plots of the iteration, are presented in the following pages.

Date: 9th - 10th April, 1962

Charcoal No.: 1

Description of Experiment: Carbon dioxide and helium only in the inlet gases at two temperatures.

Total Inlet Flow	(cc/sec.)	1.453	1.429	1.449	1.434	1.424	1.441
CO ₂ Inlet Flow	(cc/sec.)	.973	.713	.424	1.042	.696	.423
Total Outlet Flow	(cc/sec.)	1.488	1.456	1.463	1.485	1.460	1.480
CO ₂ Outlet Flow	(cc/sec.)	.934	.700	.396	.964	.644	.379
CO Outlet Flow	(cc/sec.)	.0664	.0584	.0471	.1093	.0916	.0861
CO ₂ Disappearance	(cc/sec.)	.0389	.0139	.0272	.078	.0521	.0445
CO Appearance / 2	(cc/sec.)	.0332	.0292	.0236	.0547	.0458	.0430
Average CO ₂ converted	(cc/sec.)	.0332	.0292	.0236	.0570	.0464	.0430
Temp.	(°K)	1157	1157	1157	1183	1183	1187
Reciprocal Temp.	(10 ⁻⁴ /°K)	8.64	8.64	8.64	8.45	8.45	8.42
CO ₂ converted corrected	(cc/sec.)	.0332	.0292	.0236	.0570	.0464	.0407
Reciprocal Temp.	(10 ⁻⁴ /°K)	8.64	8.64	8.64	8.45	8.45	8.45
Charcoal Mass	(10 ⁻² gm mol)	4.13	4.04	3.98	3.87	3.73	3.61
CO ₂ converted	(cc/gm mol/sec.)	.804	.723	.593	1.47	1.24	1.13
% CO ₂ in Inlet Flow		67.0	49.9	29.2	72.6	48.9	29.4

Determination of 1st Approximate Value of K₁ (using initial slope of Fig.)

$\frac{10^4}{T}$	$\frac{(ax_0)}{(b)} \ln$	$\ln(1 - \frac{ax_0}{b})$	W(avege)	a	K ₁ · 10 ⁵	log K ₁
8.64	.161	-.176	.0406	6.45 x 10 ⁻⁵	28	1.447
8.45	.236	-.270	.0376	6.40 x 10 ⁻⁵	46	1.663

Date: 5th - 6th June

Charcoal No.: 1

Description of Experiment: Carbon dioxide and carbon monoxide only in the inlet gases at two temperatures.

CO Inlet Flow	(cc/sec.)	.488	.330	.659	.919	.840	.998	.456	.214
CO ₂ Inlet Flow	(cc/sec.)	.957	1.090	.750	.481	.593	.450	.977	1.240
CO Outlet Flow	(cc/sec.)	.574	.415	.723	.953	1.012	1.182	.792	.653
CO ₂ Outlet Flow	(cc/sec.)	.910	1.038	.723	.463	.513	.383	.800	1.008
CO ₂ Disappearance	(cc/sec.)	.047	.052	.027	.018	.080	.067	.177	.232
CO Appearance / 2	(cc/sec.)	.043	.043	.032	.017	.086	.092	.168	.220
Average CO ₂ conversion	(cc/sec.)	.044	.048	.030	.017	.084	.069	.172	.226
Temp.	(°K)	1212	1211	1211	1211	1284	1285	1285	1285
Reciprocal Temp.	(10 ⁻⁴ /°K)	8.25	8.26	8.26	8.26	7.79	7.78	7.78	7.78
CO ₂ conversion corrected	(cc/sec.)	.043	.048	.030	.017	.085	.069	.172	.226
Reciprocal Temp.	(10 ⁻⁴ /°K)	8.26	8.26	8.26	8.26	7.78	7.78	7.78	7.78
Charcoal Mass	(10 ⁻² gm mol)	4.11	3.99	3.88	3.81	3.67	3.46	3.14	2.60
CO ₂ converted (cc/gm mol/sec.)		1.046	1.20	.773	.446	2.32	1.99	5.48	8.69
% CO ₂ in Inlet Flow		66.2	76.8	53.2	34.3	41.5	33.2	68.2	85.3
Smoothed CO ₂ conversion	(cc/sec.)	.041	.050	.030	.017	.090	.064	.172	.226
ax ₀ / b		.0428	.0459	.0400	.0353	.152	.142	.176	.182
1 - ax ₀ / b		.9572	.9541	.9600	.9647	.848	.858	.824	.818
ln (1 - ax ₀ / b)		-.0437	-.0470	-.0408	.0359	-.165	-.153	-.194	-.201
(2b + c) / ax ₀		58.6	50.2	72.0	111.	22.5	29.7	14.0	11.9
(2b + c) ln (1 - ax ₀ / b)		-2.56	-2.36	-2.94	-3.98	-3.71	-4.54	-2.72	-2.39
(ax ₀)									
X		-.56	-.36	-.94	-1.98	-1.71	-2.54	-.72	-.39
W/ax ₀	(10 ⁴ sec. ⁻¹)	2.25	1.79	2.90	5.02	.913	1.21	.409	.258
K ₁ (Initial Slope)(10 ⁻⁴ sec.)		7.59	7.59	7.59	7.59	27.2	27.2	27.2	27.2
WK ₁ / ax ₀		17.1	13.6	22.0	38.1	24.8	32.9	11.1	7.02
Y		15.5	12.2	19.1	34.1	22.1	29.4	9.4	5.6
K ₁ (2nd approx.)	(10 ⁻⁴ sec.)	6.76	6.76	6.76	6.76	25.4	25.4	25.4	25.4
WK ₁ / ax ₀		15.2	12.1	19.6	34.0	23.2	30.4	10.4	6.56
Y		13.6	10.7	17.7	31.0	20.5	26.9	8.7	5.2

Determination of K_1 using Extrapolated K_2 Values

Charcoal No.: 1

ax_0/b	.0341	.0410	.0557	.0536	.0678	.0861
$1 - ax_0/b$	.9659	.9590	.9443	.9464	.9322	.9139
$\ln(1 - ax_0/b)$	-.0347	-.0419	-.0573	-.0551	-.0702	-.0901
$1/x_0$	14.46	24.52	43.43	7.01	15.42	27.97
$1 - \frac{1}{x_0} \ln(1 - ax_0/b)$	1.502	2.027	3.489	1.386	2.082	3.520
$(ax_0/b)^2$	.00116	.00168	.00310	.00287	.00460	.00741
$-\left\{1 + \frac{b}{ax_0} \ln(1 - ax_0/b)\right\}$	.0175	.0211	.0289	.0278	.0354	.0456
$W/ax_0 = X$	27870	30990	37780	15510	17700	22220
K_2 (1st Approx.)	14.5	14.5	14.5	13.8	13.8	13.8
$-2(K_2 + 1)\left\{1 + \frac{b}{ax_0} \ln(1 - ax_0/b)\right\}$	.543	.654	.896	.823	1.048	1.350
Y	2.045	2.681	4.385	2.209	3.130	4.870
K_2 (2nd Approx.)	14.0	14.0	14.0	13.2	13.2	13.2
$-2(K_2 + 1)\left\{1 + \frac{b}{ax_0} \ln(1 - ax_0/b)\right\}$	.525	.633	.868	.790	1.008	1.294
Y	2.027	2.660	4.357	2.176	3.090	4.814

VALUES OF K_1 AND K_2 DURING GRAPHICAL PROCEDURE

$\frac{10^4}{T}$	8.64	8.45	8.26	7.78
Approx.	$K_1 \cdot 10^4$	K_2	K_1	K_2
1st	2.8	-	4.6	-
2nd	2.36	14.5	3.99	13.8
3rd	2.36	14.0	3.99	13.2

Date: 4th - 5th April, 1962

Charcoal No.: 3a

Description of Experiment: Carbon dioxide and helium only in the inlet gases at two temperatures.

Total Inlet Flow	(cc/sec.)	1.397	1.416	1.437	1.458	1.425	1.462
CO ₂ Inlet Flow	(cc/sec.)	1.057	.722	.461	1.062	.736	.424
Total Outlet Flow	(cc/sec.)	1.406	1.433	1.429	1.491	1.441	1.473
CO ₂ Outlet Flow	(cc/sec.)	.996	.716	.431	1.043	.720	.405
CO Outlet Flow	(cc/sec.)	.0331	.0313	.0243	.0659	.0567	.0337
CO ₂ Disappearance	(cc/sec.)	.061	.0059	.0301	.019	.0166	.0198
CO Appearance/ 2	(cc/sec.)	.0166	.0157	.0122	.0330	.0284	.0169
Average CO ₂ converted	(cc/sec.)	.0176	.0153	.0126	.0316	.0268	.0179
Temp.	(°K)	1156	1156	1156	1185	1185	1182
Reciprocal Temp.	(10 ⁻⁴ /°K)	8.66	8.66	8.66	8.44	8.44	8.46
CO ₂ converted corrected	(cc/sec.)	.0176	.0153	.0126	.0316	.0268	.0190
Reciprocal Temp.	(10 ⁻⁴ /°K)	8.66	8.66	8.66	8.44	8.44	8.44
Charcoal Mass	(10 ⁻² gm mol)	4.14	4.11	4.07	4.01	3.93	3.86
CO ₂ converted (cc/gm mol/sec.)		.425	.372	.310	.788	.682	.492
% CO ₂ in Inlet Flow		75.7	51.0	32.1	72.8	51.7	29.0

Determination of 1st Approximate Value of K_1 (using initial slope of Fig.)

$\frac{10^4}{T}$	$\left(\frac{ax_0}{b}\right)_{\text{lim}}$	$\ln(1 - ax_0/b)$	W(avge)	a	$K_1 \cdot 10^5$	log K_1
8.66	.057	-.0586	.0412	6.33×10^{-5}	9	5.954
8.44	.0765	-.0795	.0395	6.46×10^{-5}	13	4.114

DETERMINATION OF K_1 CHARCOAL NO. 3a

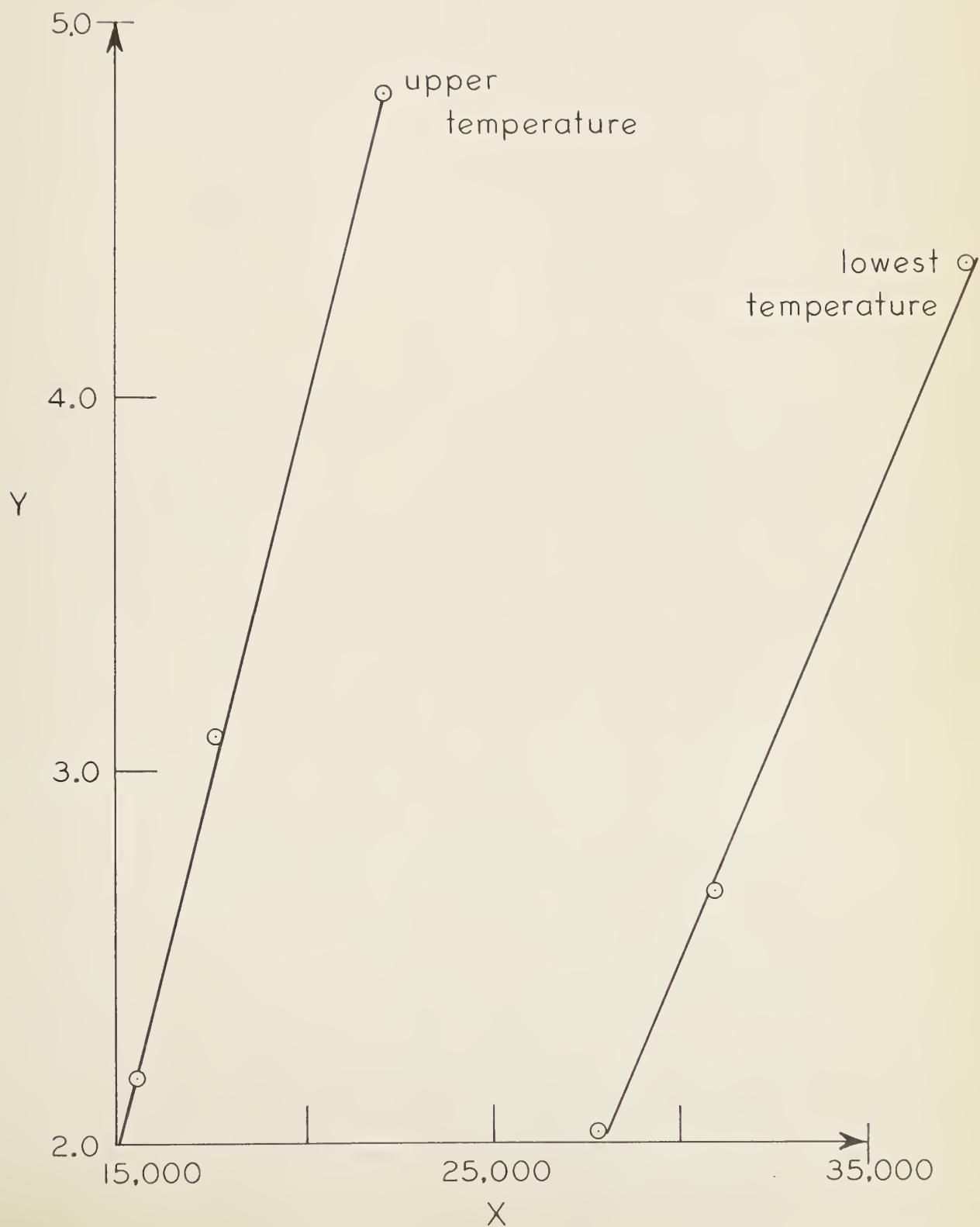


FIGURE 33

ARRHENIUS PLOT FOR K₁ CHARCOAL NO.3a

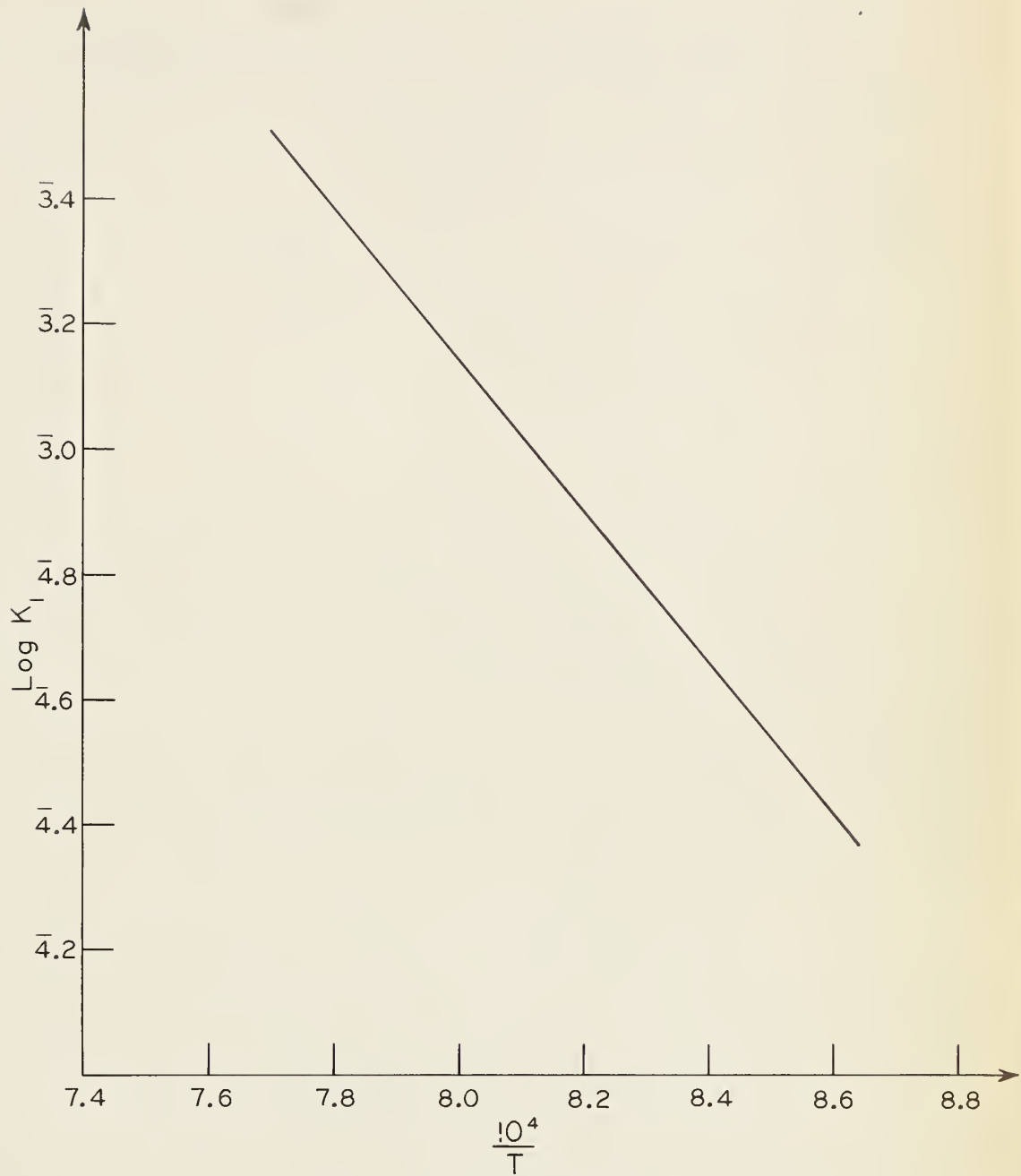


FIGURE 34

DETERMINATION OF K_2 CHARCOAL NO. 3a

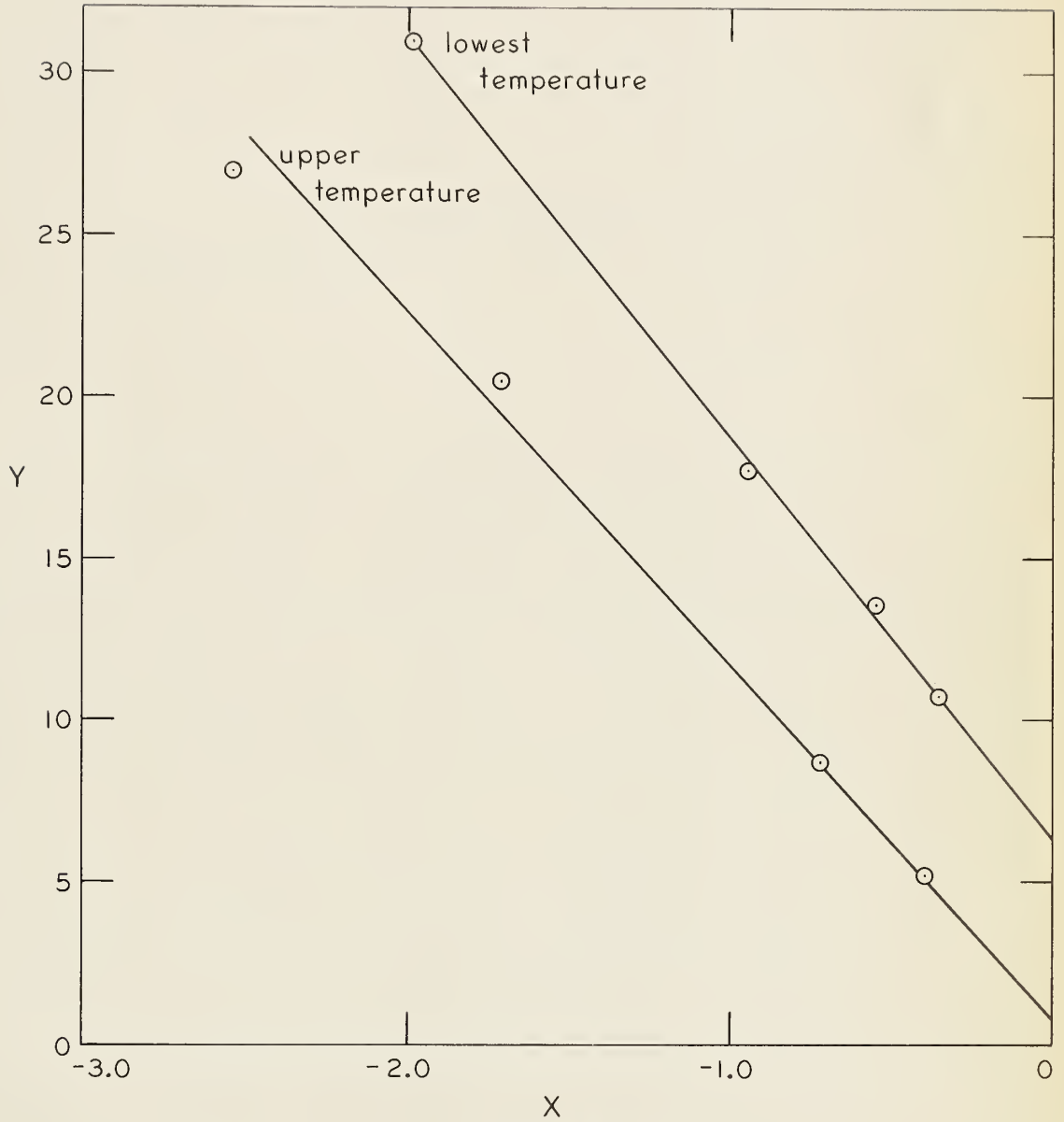


FIGURE 35

ARRHENIUS PLOT FOR K₂ CHARCOAL NO.3a

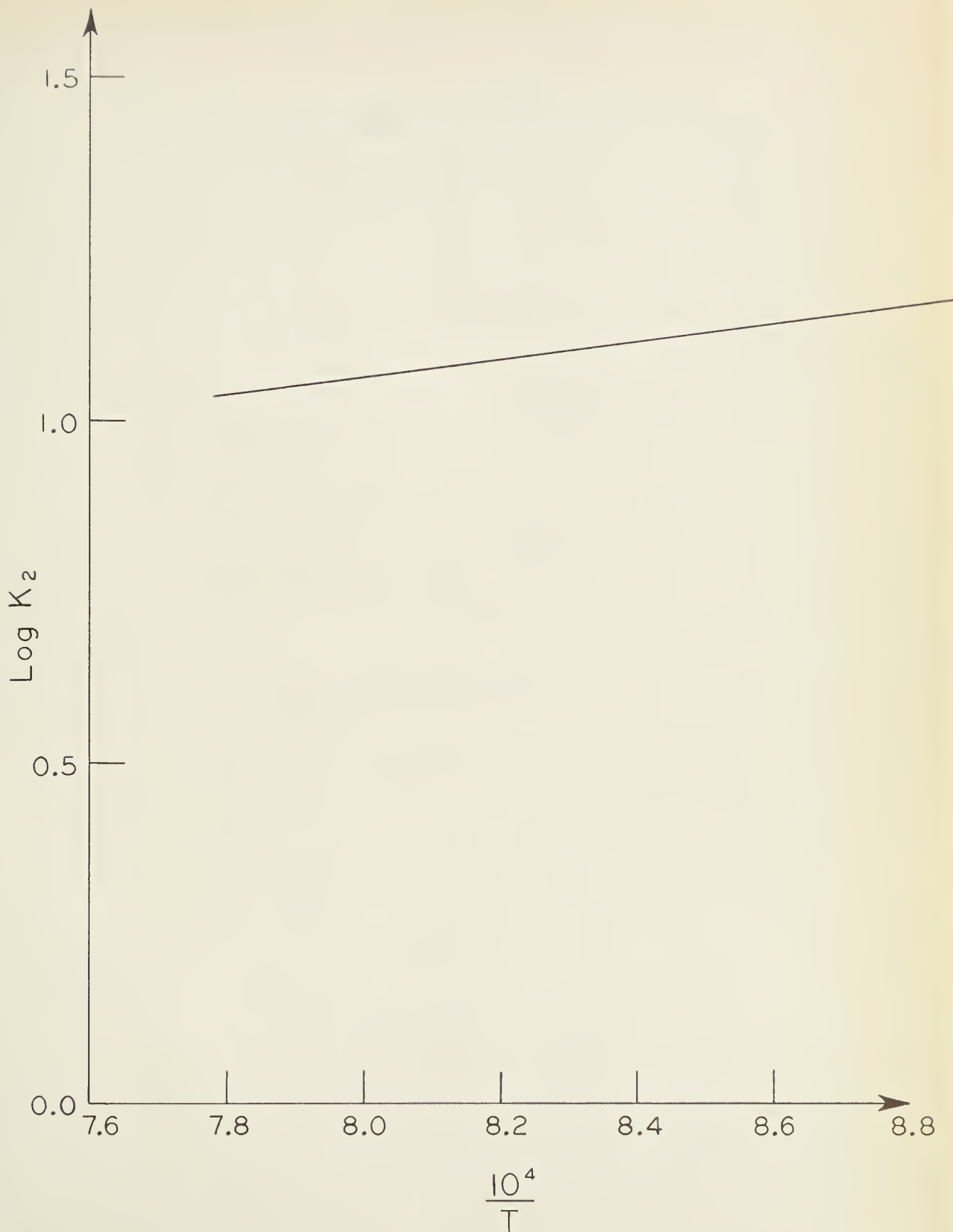


FIGURE 36

Date: 11th - 16th May, 1962

Charcoal No.: 3a

Description of Experiment: Carbon dioxide and carbon monoxide only in the inlet gases
at two temperatures.

CO Inlet Flow	(cc/sec.)	.353	.182	.804	.343	.437	1.015
CO ₂ Inlet Flow	(cc/sec.)	1.003	1.230	.633	1.102	.983	.443
CO Outlet Flow	(cc/sec.)	.425	.268	.842	.638	.674	1.106
CO ₂ Outlet Flow	(cc/sec.)	.972	1.182	.611	.944	.870	.410
CO ₂ Disappearance	(cc/sec.)	.031	.048	.022	.158	.114	.033
CO Appearance / 2	(cc/sec.)	.036	.043	.019	.147	.118	.045
Average CO ₂ conversion	(cc/sec.)	.034	.046	.020	.150	.117	.034
Temp°K		1205	1207	1209	1271	1271	1272
Reciprocal Temp.	(10 ⁻⁴ °K ⁻¹)	8.30	8.29	8.27	7.87	7.87	7.86
CO ₂ conversion corrected	(cc/sec.)	.034	.045	.018	.152	.119	.034
Reciprocal Temp.	(10 ⁻⁴ °K ⁻¹)	8.30	8.30	8.30	7.86	7.86	7.86
Charcoal Mass	(10 ⁻² gm mol)	4.01	3.91	3.82	3.60	3.24	2.75
CO ₂ converted	(cc/gm mol/sec.)	.848	1.151	.471	4.22	3.67	1.24
% CO ₂ in Inlet Flow		74.0	87.2	44.0	76.2	69.2	30.4
Smoothed CO ₂ conversion	(cc/sec.)	.036	.045	.017	.152	.119	.034
ax ₀ /b		.0359	.0366	.0269	.138	.121	.0767
1 - ax ₀ /b		.9641	.9634	.9731	.862	.879	.9233
ln (1 - ax ₀ /b)		-.0366	-.0373	-.0273	-.149	-.129	-.0798
(2b + c) / ax ₀		65.5	58.7	122.	16.8	20.2	55.9
($\frac{2b+c}{ax_0}$) ln ($\frac{1-ax_0}{b}$)		-2.40	-2.19	-3.33	-2.50	-2.61	-4.46
X		-.40	-.19	-1.33	-.50	-.61	-2.46
W/ax ₀	(10 ⁴ sec. ⁻¹)	2.50	1.95	5.03	.531	.610	1.81
K ₁ (initial slope)	(10 ⁻⁴ sec.)	1.65			3.47		
WK ₁ /ax ₀		4.13	3.22	8.30	1.84	2.12	6.28
Y		2.73	2.03	5.97	.34	.51	2.82
K ₁ (2nd Approx.)	(10 ⁻⁴ sec.)	1.65			3.34		
WK ₁ /ax ₀					1.77	2.04	6.05
Y					.27	.43	2.59

Determination of K₁ using Extrapolated K₂ Values

Charcoal No.: 3a

ax ₀ /b		.0167	.0212	.0273	.0298	.0364	.0448
1 - ax ₀ /b		.9833	.9788	.9727	.9702	.9636	.9552
ln (1 - ax ₀ /b)		-.0169	-.0214	-.0277	-.0303	-.0371	-.0458
1/x ₀		19.3	45.4	77.5	12.5	25.7	54.6
1 - 1/x ₀ ln (1 - ax ₀ /b)		1.326	1.972	3.147	1.379	1.953	3.501
(ax ₀ /b) ²		.00028	.00045	.00075	.00089	.00132	.00201
($1 + \frac{b}{ax_0} \ln (1 - ax_0/b)$)		.00844	.0108	.0139	.0152	.0186	.0231
W/ax ₀ = X		52690	60170	72360	28430	32850	45510
K ₂ 1st Approx.		7.81			4.71		
- 2 (K ₂ + 1) ($1 + \frac{b}{ax_0} \ln (1 - ax_0/b)$)		.149	.190	.245	.174	.212	.264
Y		1.475	2.162	3.392	1.553	2.165	3.765
K ₂ 2nd Approx.		8.20			4.81		
		.155	.199	.256	.177	.216	.268
Y		1.481	2.171	3.403	1.556	2.169	3.769

VALUES OF K_1 AND K_2 DURING GRAPHICAL PROCEDURE

$\frac{10^4}{T}$	8.66		8.44		8.30		7.86	
<u>Approx.</u>	$K_1 \cdot 10^4$	K_2	K_1	K_2	K_1	K_2	K_1	K_2
1st	.9		1.3		1.65	3.45	3.47	1.26
2nd	.93	7.81	1.31	4.71	1.65	3.45	3.34	1.18
3rd	.93	8.20	1.31	4.81				

DETERMINATION OF K_1 CHARCOAL NO. 1

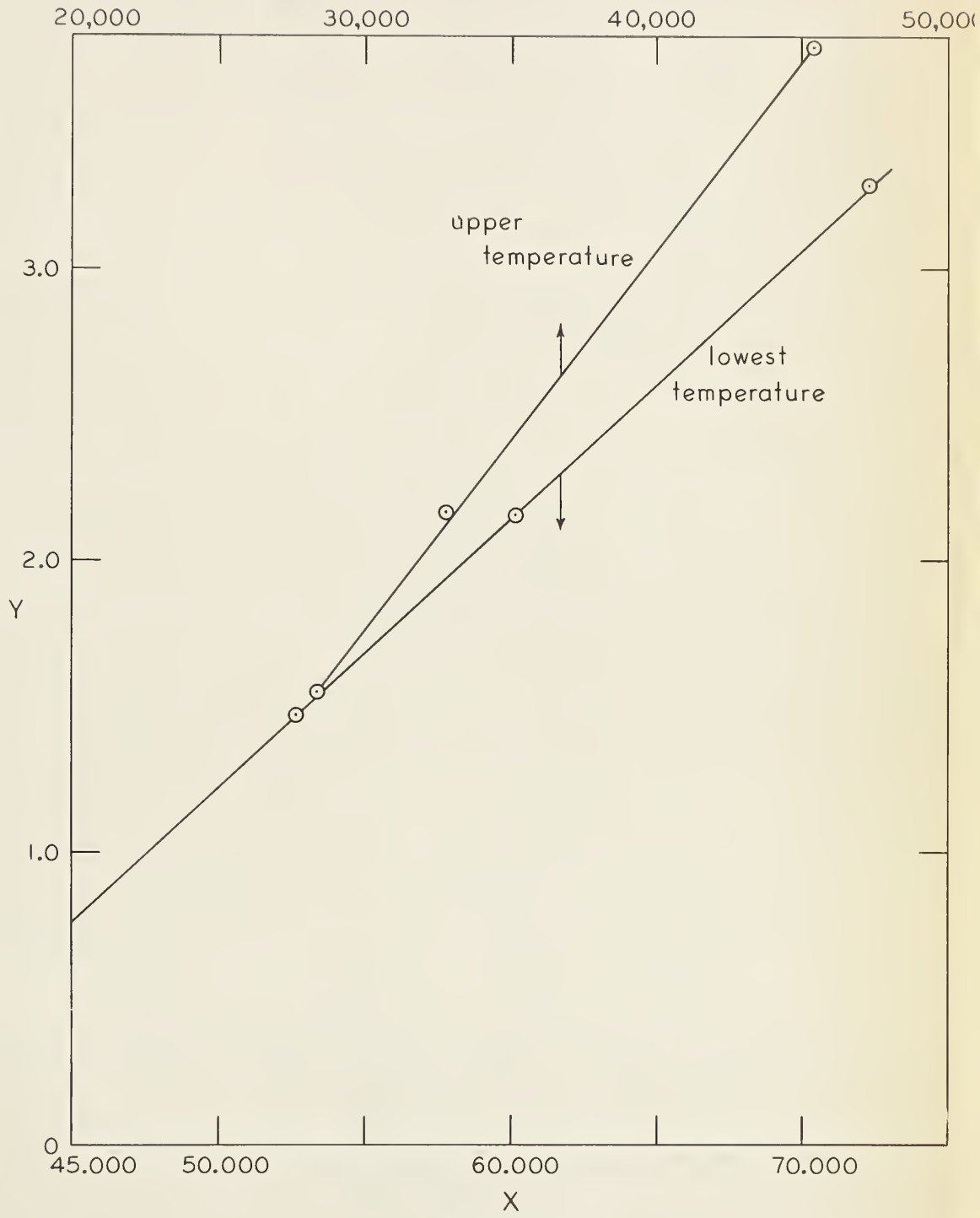


FIGURE 37

ARRHENIUS PLOT FOR K_1 CHARCOAL NO.1

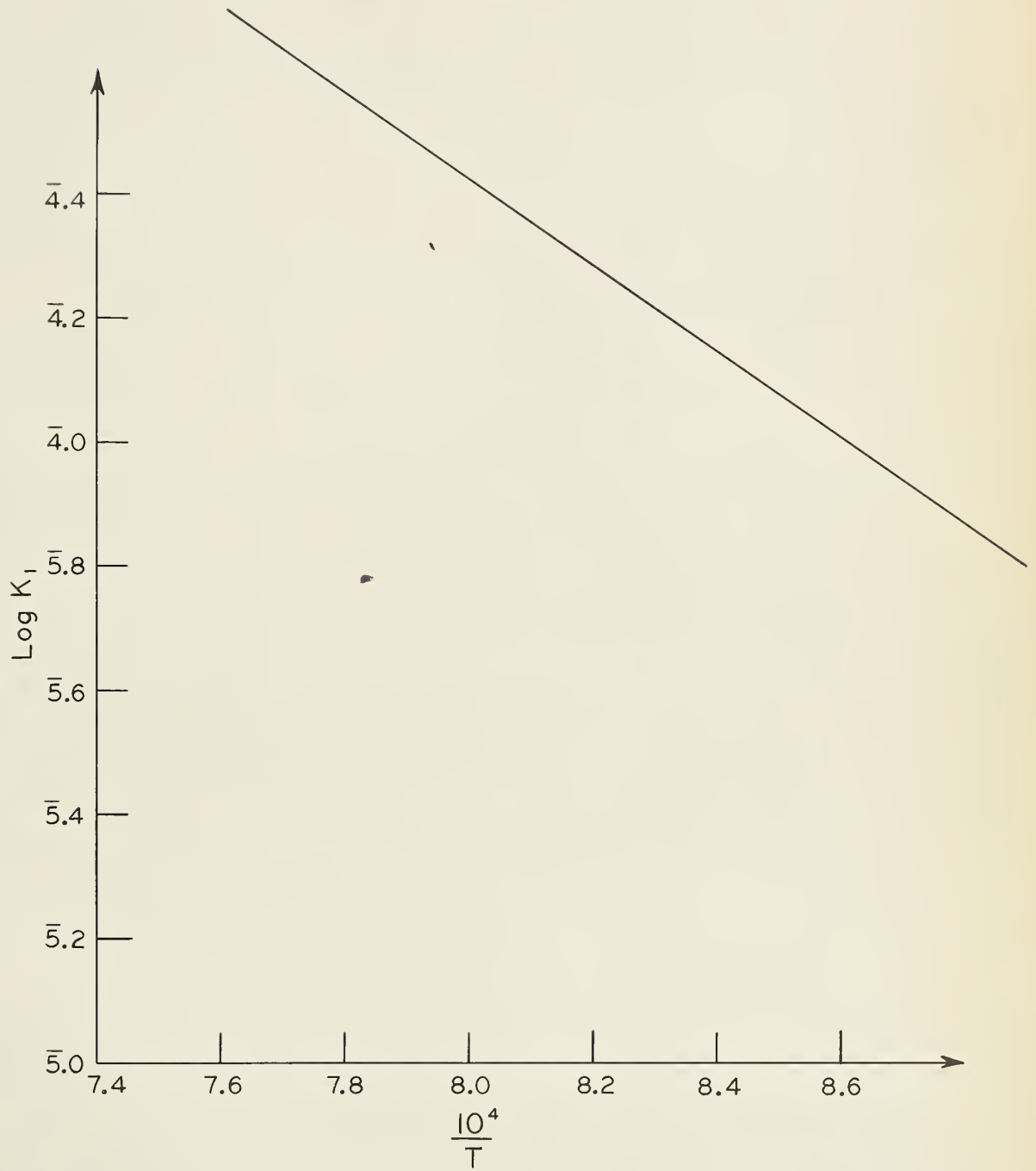


FIGURE 38

DETERMINATION OF K_2 CHARCOAL NO. 1

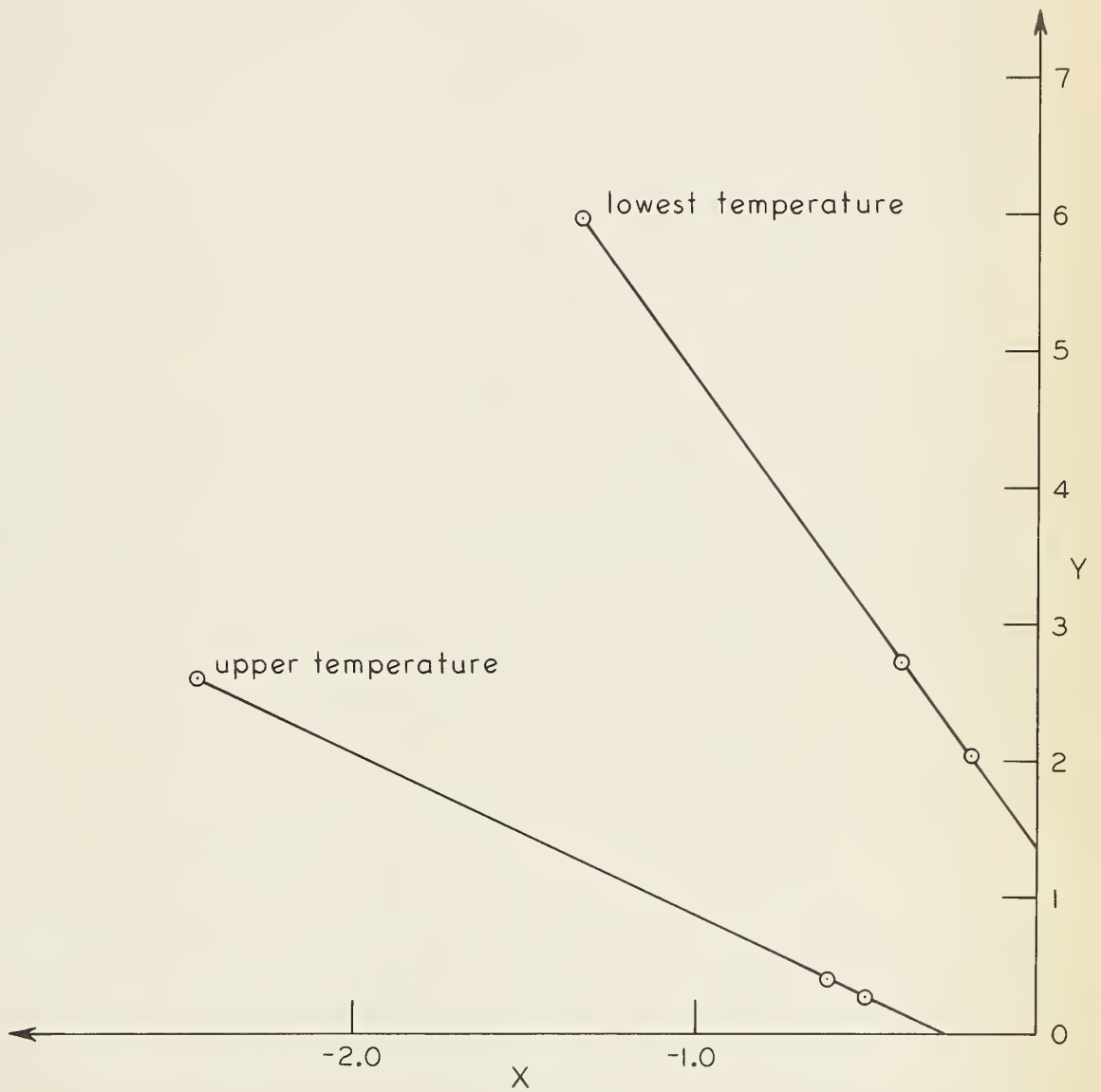


FIGURE 39

ARRHENIUS PLOT FOR K₂ CHARCOAL NO.1

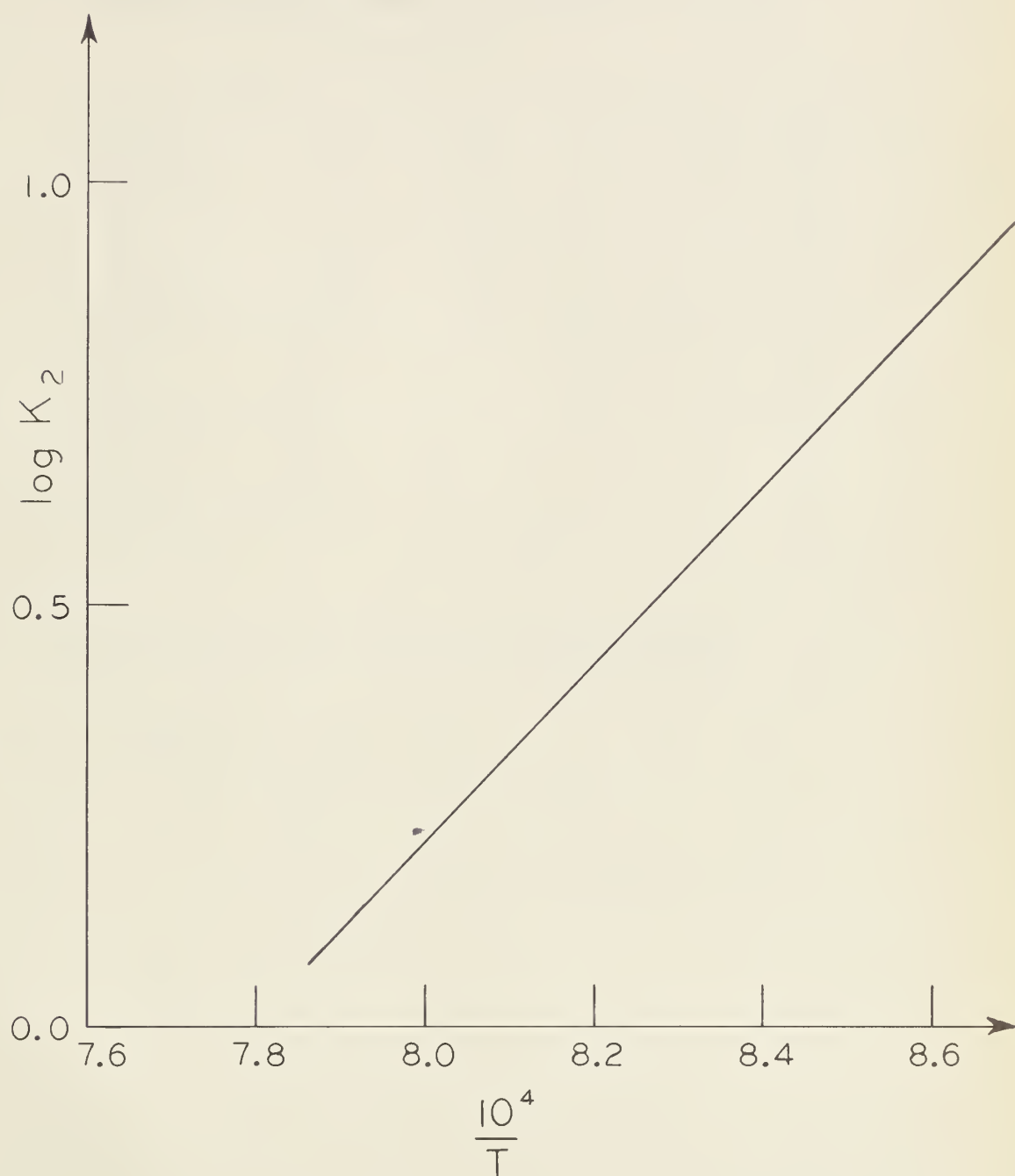


FIGURE 40

Date: 12th - 13th April

Charcoal No.: 4

Description of Experiment: Carbon dioxide and helium only in the inlet gases

at two temperatures.

Total Inlet Flow	(cc/sec.)	1.438	1.434	1.408	1.444	1.444	1.480
CO ₂ Inlet Flow	(cc/sec.)	.988	.657	.422	1.073	.645	.423
Total Outlet Flow	(cc/sec.)	1.449	1.447	1.417	1.483	1.461	1.492
CO ₂ Outlet Flow	(cc/sec.)	.968	.645	.396	1.030	.617	.393
CO Outlet Flow	(cc/sec.)	.0373	.0304	.0226	.0783	.0523	.0440
CO ₂ Disappearance	(cc/sec.)	.020	.012	.026	.043	.028	.030
CO Appearance/ 2	(cc/sec.)	.0187	.0152	.0113	.0392	.0262	.0220
Average CO ₂ converted	(cc/sec.)	.0188	.0147	.0121	.0396	.0264	.0220
Temp.	(°K)	1164	1165	1165	1195	1194	1195
Reciprocal Temp.	(10 ⁻⁴ °K ⁻¹)	8.59	8.58	8.58	8.37	8.38	8.37
CO ₂ converted corrected	(cc/sec.)	.0190	.0147	.0121	.0396	.0274	.0220
Reciprocal Temp.	(10 ⁻⁴ °K ⁻¹)	8.58	8.58	8.58	8.37	8.37	8.37
Charcoal Mass	(10 ⁻² gm mol)	4.14	4.10	4.06	3.99	3.90	3.84
CO ₂ converted	(cc/gm mol/sec.)	.459	.359	.298	.992	.703	.572
% CO ₂ in Inlet Flow		68.7	45.8	30.0	74.3	44.7	28.6

Determination of 1st Approximate Value of K₁ (using initial slope of Fig.)

$\frac{10^4}{T}$	(ax_0) ($\frac{1}{b}$) lim	$\ln(1 - \frac{ax_0}{b})$	W(avge)	a	$K_1 \cdot 10^5$	log K ₁
8.58	.0442	-.0452	.0411	6.37×10^{-5}	7	$\bar{5}.845$
8.37	.0703	-.0726	.0393	6.50×10^{-5}	12	$\bar{4}.079$

Date: 22nd - 23rd May, 1962

Charcoal No.: 4

Description of Experiment: Carbon dioxide and carbon monoxide only in the inlet gases
at two temperatures.

CO Inlet Flow	(cc/sec.)	.402	.287	.803	.714	.511	1.013
CO ₂ Inlet Flow	(cc/sec.)	1.060	1.184	.647	.695	.987	.466
CO Outlet Flow	(cc/sec.)	.484	.345	.822	.990	.804	1.147
CO ₂ Outlet Flow	(cc/sec.)	1.013	1.139	.632	.548	.780	.396
CO ₂ Disappearance	(cc/sec.)	.047	.045	.015	.147	.207	.070
CO Appearance / 2	(cc/sec.)	.041	.029	.010	.138	.147	.067
Average CO ₂ conversion	(cc/sec.)	.043	.045	.014	.142	.177	.068
Temp.	(°K)	1214	1213	1210	1275	1275	1275
Reciprocal Temp.	(10 ⁻⁴ °K ⁻¹)	8.24	8.24	8.26	7.84	7.84	7.84
CO ₂ conversion corrected	(cc/sec.)	.043	.046	.015	.142	.177	.068
Reciprocal Temp.	(10 ⁻⁴ °K ⁻¹)	8.24	8.24	8.24	7.84	7.84	7.84
Charcoal Mass	(10 ⁻² gm mol)	2.69	2.57	2.49	3.98	3.55	2.92
CO ₂ converted	(cc/gm mol/sec.)	1.60	1.79	.602	3.57	4.99	2.33
% CO ₂ in Inlet Flow		72.5	80.5	44.6	49.3	65.0	31.3
Smoothed CO ₂ conversion	(cc/sec.)	.041	.048	.018	.146	.181	.068
ax ₀ /b		.0386	.0405	.0280	.210	.183	.146
1 - ax ₀ /b		.9614	.9595	.9720	.790	.817	.854
ln (1 - ax ₀ /b)		-.0394	-.0414	-.0284	-.236	-.202	-.158
(2b + c) / ax ₀		61.7	55.3	114.	14.4	13.7	28.6
(2b + c) ln (1 - ax ₀ /b)		-2.43	-2.29	-3.28	-3.40	-2.77	-4.52
($\frac{2b+c}{ax_0}$) X		-.43	-.29	-1.28	-1.40	-.77	-2.52
W/ax ₀	(10 ⁴ sec. ⁻¹)	1.47	1.20	3.09	.611	.439	.962
K ₁ (Initial Slope)	(10 ⁻⁴ sec.)	1.66			4.57		
WK ₁ /ax ₀		2.44	1.99	5.13	2.79	2.00	4.40
Y		1.01	.70	2.85	.39	.23	.89

Determination of K₁ using Extrapolated K₂ Values

Charcoal No.: 4

ax ₀ /b	.0194	.0234	.0279	.0365	.0441	.0487
1 - ax ₀ /b	.9806	.9766	.9721	.9635	.9559	.9513
ln (1 - ax ₀ /b)	-.0196	-.0237	-.0283	-.0372	-.0451	-.0499
1/x ₀	23.4	50.5	83.6	9.46	28.0	51.3
1 - $\frac{1}{x_0}$ ln (1 - ax ₀ /b)	1.459	2.197	3.366	1.352	2.263	3.560
(ax ₀ /b) ²	.00038	.00055	.00078	.00133	.00194	.00237
$-\left(\frac{1+b}{ax_0} \ln \left(1 - \frac{ax_0}{b}\right)\right)$	.0098	.0119	.0142	.0187	.0227	.0244
W/ax ₀ = X	48300	59640	77070	22800	30650	41760
K ₂ (1st Approx.)	10.1	10.1	10.1	4.07	4.07	4.07
$-2(K_2 + 1) \left(\frac{1+b}{ax_0} \ln \left(1 - \frac{ax_0}{b}\right)\right)$	.218	.264	.315	.190	.230	.247
Y	1.677	2.461	3.681	1.542	2.493	3.807

VALUES OF K₁ AND K₂ DURING GRAPHICAL PROCEDURE

$\frac{10^4}{T}$	8.58	8.37	8.24	7.84
Approx.	K ₁ ^{10⁴}	K ₂	K ₁	K ₂
1st	.7		1.2	1.66
2nd	.70	10.1	1.2	4.07

DETERMINATION OF K_1 CHARCOAL NO. 4

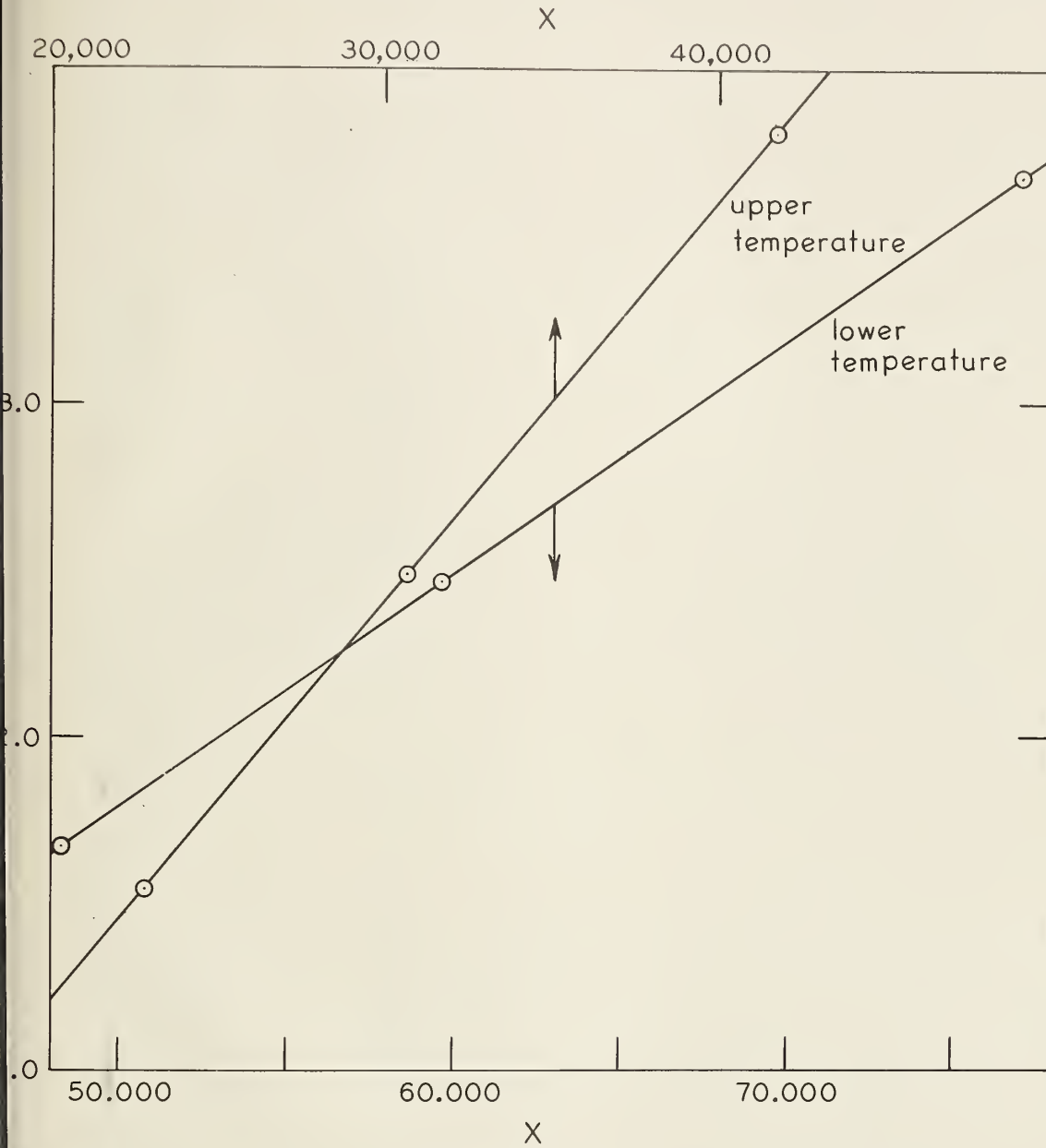


FIGURE 41

ARRHENIUS PLOT FOR K_1 , CHARCOAL NO.4

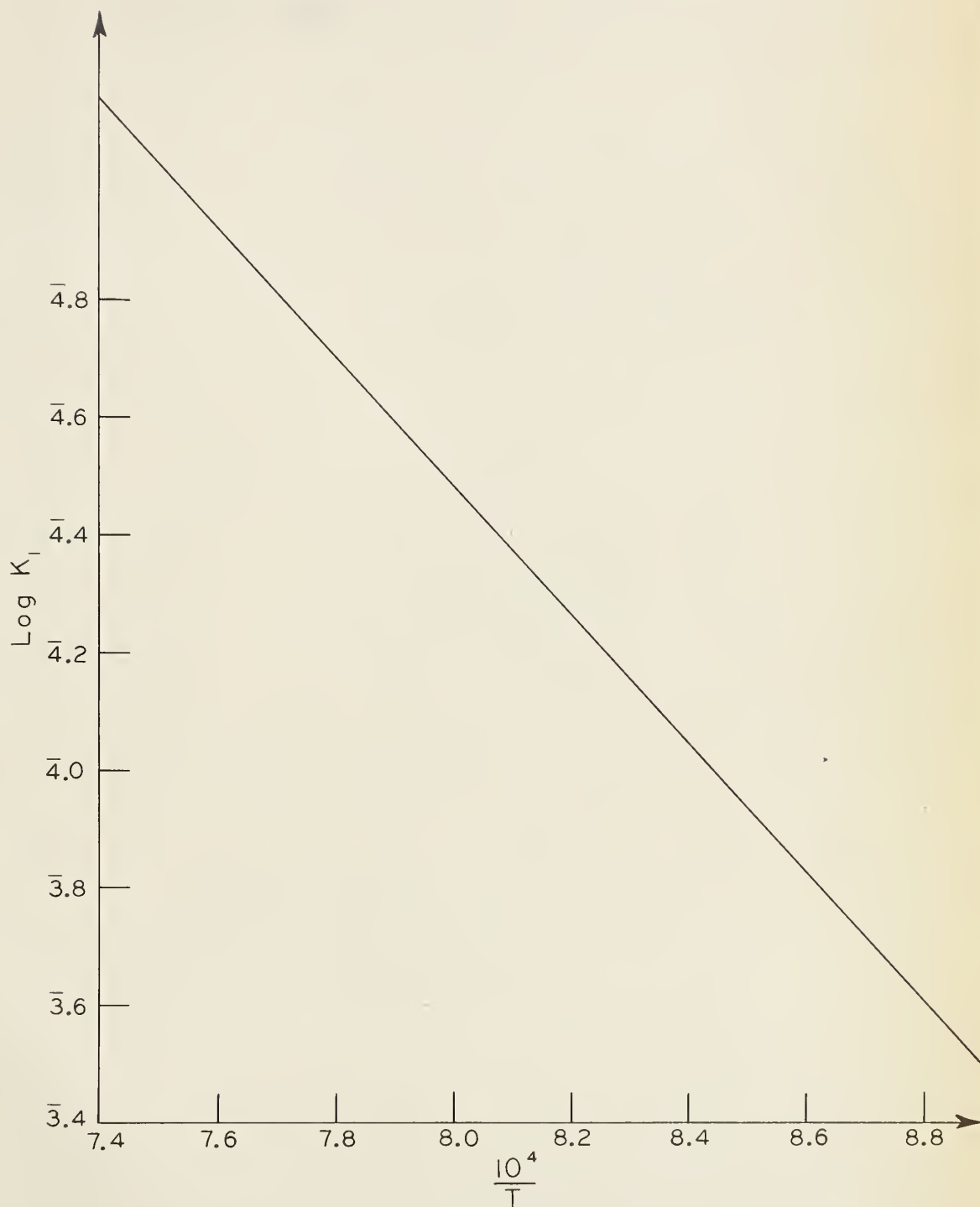


FIGURE 42

DETERMINATION OF K_2 CHARCOAL NO. 4

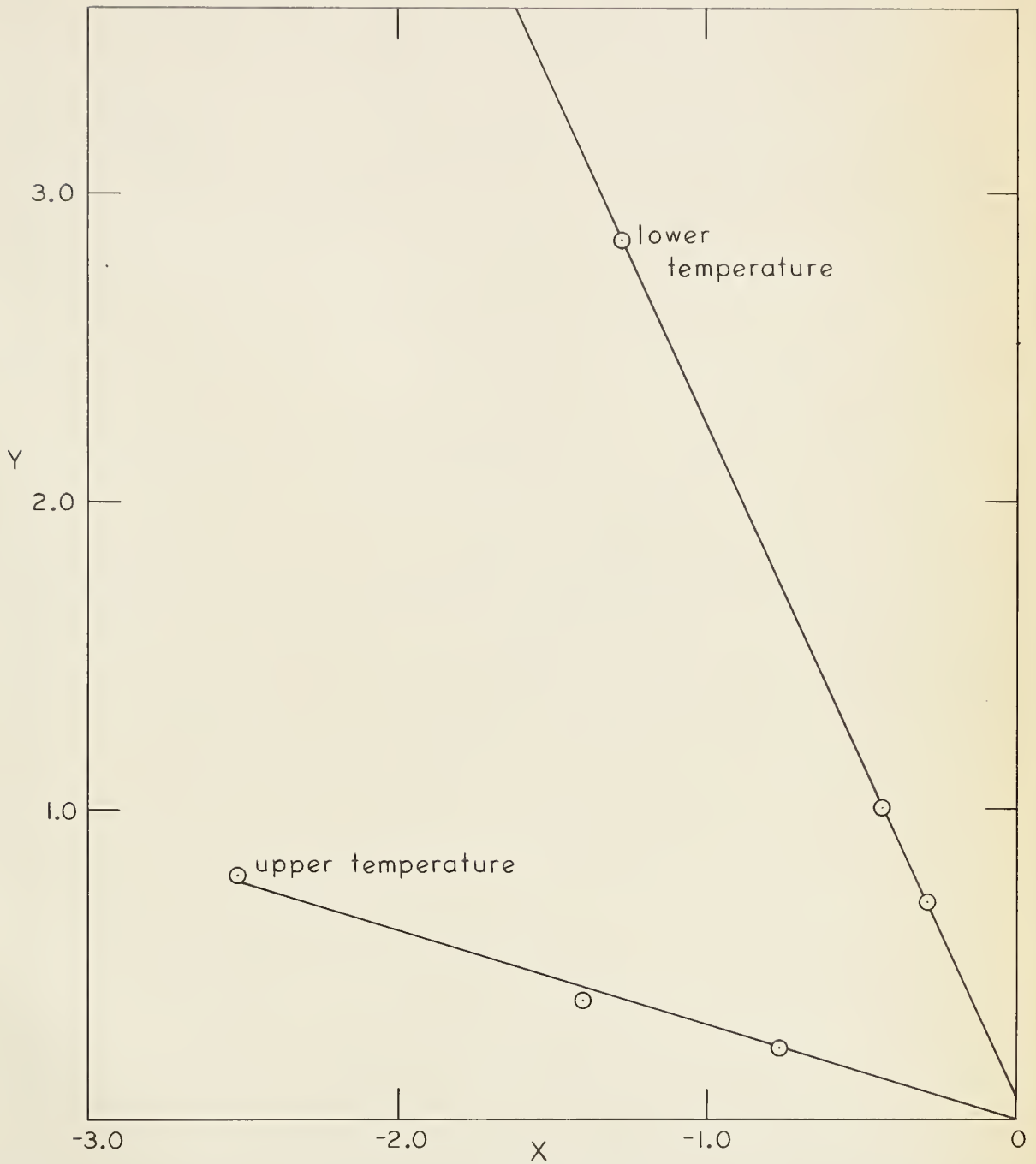


FIGURE 43

ARRHENIUS PLOT FOR K₂ CHARCOAL NO.4



FIGURE 44

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